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Waste Crankcase Oil Heater Study Phase 2. Organic and Inorganic Speciation Analyses

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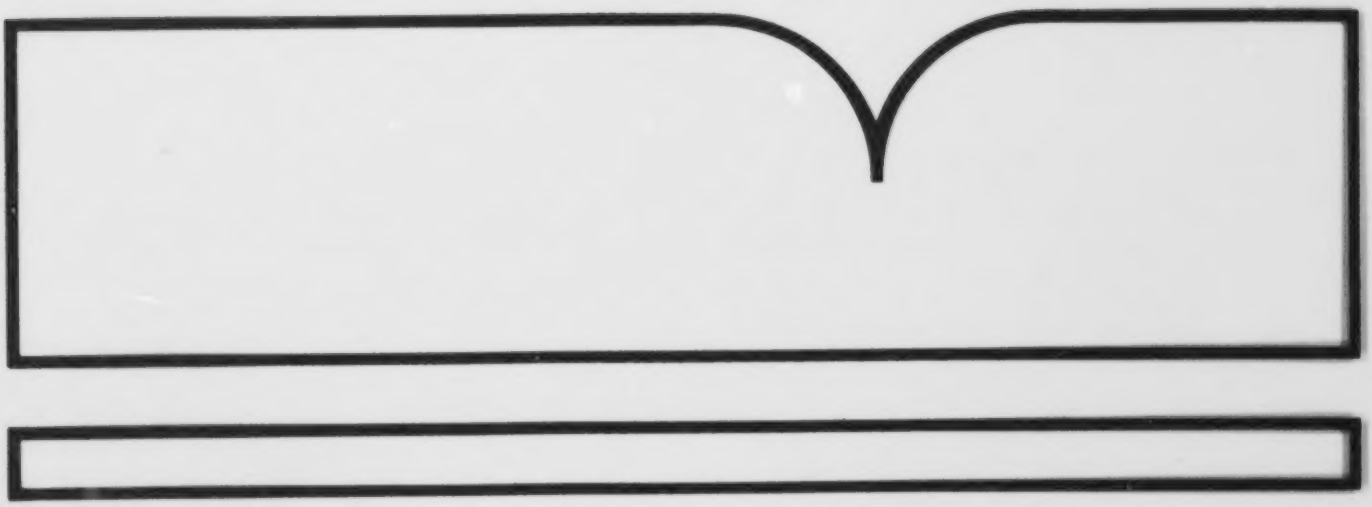

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WASTE CRANKCASE OIL HEATER STUDY: PHASE II. ORGANIC AND INORGANIC SPECIATION ANALYSES

by

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16. ABSTRACT The report gives results of measurements of specific chemical species in emissions from two waste-oil-fired commercial heaters. The species were identified earlier in a Level 1 analysis of similar emissions. One heater utilized a vaporizing pot, and the other, an air atomization combustion chamber. Polynuclear aromatic hydrocarbons (PAHs) were analyzed in gaseous emissions from both units. Elemental analyses (including Pb, Fe, Cd, Zn, Cl, and Br) were performed on the air atomization discharges. Analyses also were conducted on these emissions to measure possible organolead constituents and to determine the distribution of iron oxidation states (Fe(II) versus Fe(III)). In addition, several waste crankcase oils were tested for the elemental species of interest to establish baseline levels for emission data and to determine the effect on metal concentrations of both filtration and sedimentation during storage. Elevated levels of PAHs were found in emissions from both heaters. Elevated levels of metallic species also were found, and Fe(III) was determined to be the major form of iron in combustion emissions from the waste-oil-fired air atomization heater. Since combinations of certain PAHs and Fe(III) have been shown to promote certain types of mammalian cancers, these results indicate a potentially serious health hazard.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Aromatic Polynuclear Hydrocarbons	Pollution Control	13B	
Lubricating Oils		Stationary Sources	11H	07C
Wastes	Metals	Waste Crankcase Oils	14G	11F, 07B
Crankcases	Carcinogens		21J	06E
Heating Equipment	Toxicity		13A	06T
Combustion	Measurement		21B	14B

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ABSTRACT

This study was designed to measure specific chemical species in emissions from two waste oil-fired residential heating appliances. The species under investigation had been identified previously in a Level 1 analysis of similar emissions. The two combustion systems tested utilized a vaporizing pot and air atomization combustion chamber designs. Polynuclear aromatic hydrocarbons (PAH) were analyzed in gaseous emissions from both units. Elemental analyses, including Pb, Fe, Cd, Zn, Cl, and Br, were performed on the air atomization discharges. Analyses also were conducted on these emissions to measure possible organolead constituents and to determine the distribution of iron oxidation states (Fe(II) versus Fe(III)). In addition, several waste crankcase oils were tested for the elemental species of interest to establish baseline levels for emission data and to determine the effect of filtration and of sedimentation on metal concentrations during storage.

Elevated levels of PAH were found in emissions from both heaters. Elevated levels of metallic species also were found and Fe(III) was determined to be the major form of iron in combustion emissions from the waste oil-fired air atomization heater. Since combinations of certain PAH and Fe(III) have been shown to promote certain types of mammalian cancer, these results indicate a potentially serious health hazard over and above the normal health concerns associated with PAH and metal combustion emissions.

CONTENTS

Abstract. iii
Figures vi
Tables. viii
Acknowledgements. ix

1. Introduction. . . . . .
   Scope and results of Phase I study. 1
   Phase II objective. 2
2. Conclusions 3
   Particulate emissions 3
   PAH emissions 3
   Organolead compounds. 4
   Fuel samples. 4
3. Recommendations for Future Research 5
4. Experimental Methods and Procedures 6
   Sampling procedures 6
   Analytical methods. 12
5. Results and Discussion. 22
   Waste oils. 22
   Particulate emissions 29
   Organolead compounds. 39

References. 42
Appendices

A. XRF spectra of waste oil samples. 44
B. XRF spectra of air atomizer particulate discharges. 52

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FIGURES

Number		Page
1	Test combustion systems.	7
2	Modified Method 5 sampling train	11
3	Cryogenic sampling train for collecting volatile organometallic emissions.	13
4	Gas chromatogram of PAH standard mixture	17
5	Gas chromatograph interface to the atomic absorption spectrometer burner head.	18
6	Chromatograms of tetralkyl lead compounds in the GC/AAS system .	20
7	Spectrum of automobile oil samples (AT) using Dy target.	24
8	Spectrum of automobile waste oil sample (AB) using Dy target . .	25
9	Spectrum of truck waste oil sample (TT) using Dy target.	26
10	Spectrum of truck waste oil sample (TB) using Dy target.	27
11	Spectrum of automobile waste oil sample (DF) using Dy target . .	28
12	Spectrum for particulate sample #3 obtained with a Dy target . .	31
13	Spectrum for particulate sample #3 obtained with a Fe target . .	32
14	HRGC/MS total ion chromatogram of vaporizing pot sample.	36
15	HRGC/MS chromatogram of air atomization emission sample.	37
16	GC/AAS chromatogram of the spiked waste oil fuel by direct injection.	40

Number		Page
A-1	Spectrum of waste oil sample AB using a Ge target.	45
A-2	Spectrum of waste oil sample AT using a Ge target.	46
A-3	Spectrum of waste oil sample TT using a Ge target.	47
A-4	Spectrum of waste oil sample TB using a Ge target.	48
A-5	Spectrum of waste oil sample DF using a Ge target.	49
A-6	Spectrum of waste oil sample MST2 using a Ge target.	50
A-7	Spectrum of waste oil sample MST2 using a Dy target.	51
B-1	Spectrum for particulate sample #5 using a Dy target	53
B-2	Spectrum for particulate sample #5 using a Fe target	54
B-3	Spectrum for particulate sample #6 using a Dy target	55
B-4	Spectrum for particulate sample #6 using a Fe target	56

TABLES

Number		Page
1	Waste oil sample history.	8
2	Test conditions for vaporizing pot combustion experiments	9
3	Test conditions for air atomization combustion experiments. . . .	10
4	Source and composition of solid synthetic standard.	15
5	Alkyl lead reference mixture - MLA-500(T313).	19
6	Synthetic standard for waste oils	21
7	Results of X-ray fluorescence analysis of waste oils.	23
8	Results of X-ray fluorescence analysis of particulates.	30
9	Ferrous ion content of filter samples	33
10	Results of PAH analyses	34
11	Comparison of benzo(a)pyrene concentrations reported in raw fuels and combustion emissions.	38

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SECTION 1

INTRODUCTION

SCOPE AND RESULTS OF PHASE I STUDY

The work reported here is an extension of an earlier investigation on residential heating appliances designed specifically for waste oil combustion (1,2). In that Phase I study, two types of waste oil heaters were tested while firing filtered--but otherwise untreated--waste crankcase oils. One of the heaters tested was a Kroll, Model W400L, waste oil heater rated at 35.2 kW (120,000 Btu/hr heat input). This heater uses a vaporizing pot burner in which only the heated vaporized fuel is combusted. With this type of burner, the residue of unburned material which accumulates in the bottom of the fuel pot must be physically removed. The other unit tested, a Dravo Hastings Thermoflo, Model 20-WO, waste oil heater, rated at 73.3 kW (250,000 Btu/hr heat input), uses a low pressure air atomizing burner. With this type of burner, most of the fuel is burned and discharged as stack effluent.

The combustion of both truck and automotive waste crankcase oils was examined in each heater, resulting in four test runs. During each of these four test runs, the stack was sampled by two different techniques: the Source Assessment Sampling System (SASS) train and a dilution tunnel, thus producing eight sets of sampling data. Specifically, the following analyses were performed:

- Level 1 analysis of four SASS trains, four sets of dilution filters and two samples of pot residue
- Determination of heating value, moisture, ash, viscosity, and C, H, N, and S analysis of the two waste oils
- Inductively coupled argon plasma (ICAP) analysis for 28 elements on 20 combustion samples and two waste oils.

Results of these analyses were used to compare the two burner systems, the automotive and truck waste oils, and the two types of emission sampling techniques.

The air atomizing burner yielded higher gas-phase concentrations of most inorganic species than the vaporizing pot combustion system. In both combustion systems, the time-weighted-average, Threshold Limit Values (TLVs) were exceeded for several elemental species. Although direct correlation of TLVs would require analysis of specific species rather than the elemental analyses performed in this study, the magnitude by which the TLVs were exceeded causes serious concern that harmful levels of metals may be discharged in the gaseous emissions from

the heaters. Results suggested the presence of polynuclear aromatic hydrocarbons (PAH) in both types of combustion systems. These compounds also can pose a serious health hazard.

Fuel analyses revealed generally higher concentrations of metallic species in the automotive oil. This high metal content also was reflected in the combustion emissions from the automotive fuel, which showed higher metal concentrations than the truck waste oil emissions. Total organic concentrations were similar for the two fuels, although chemical composition of the organic discharges was different.

The SASS train collected larger amounts of the elemental discharges than the dilution tunnel, in most cases. This effect also was observed for organic emissions. The SASS train incorporates a cooled resin bed positioned after the heated filter. The resin bed is effective in collecting organic constituents, especially semivolatile compounds that may not be retained on the dilution tunnel filter.

PHASE II OBJECTIVE

Phase I results indicated that the use of waste crankcase oil in residential heaters produces high levels of metallic discharges and possibly significant levels of PAH, both of which could pose significant health hazards. Since several researchers have proposed the use of waste oil, either as a direct fuel or as a blending agent to lower the cost of primary fuels (3,4), investigating the environmental impacts of expanded waste oil usage is important.

The objective of the Phase II study was to perform detailed investigations on waste oil emission species identified or suspected from Level 1 data generated in the earlier program. The experimental portion of this study consisted of five parts:

(1) Analysis of polynuclear aromatic hydrocarbons (PAH) in gaseous emissions from a vaporizing pot heater (Kroll) and an air atomization combustion system (Dravo).

(2) X-ray fluorescence analysis of inorganic species, including Br, I, Fe, Cd, Pb, and Zn, in particulate discharges from the air atomization heater.

(3) Analysis of the Fe(II)/Fe(III) ratio in the air atomization gaseous effluent.

(4) Analysis of air atomization gaseous discharges for organolead composition.

(5) Analyses of five separate fuels to determine the metal content as a function of storage, batch differences, and fuel sources.

The fuel used in this program was obtained from a service station and is typical of used automobile crankcase oil.

SECTION 2

CONCLUSIONS

The conclusions from this study can be summarized according to the four substances investigated: particulate emissions, PAH emissions, organolead compounds, and fuel samples.

PARTICULATE EMISSIONS

- Analysis of elemental species in emission samples from the air atomization heater confirmed the elevated metal content of waste oil emissions previously identified in the Phase I study.
- Bromine levels were exceptionally high indicating that bromine from gasoline antiknocking additives exists as a major constituent of waste crankcase oil and represents a major air emissions constituent from this source.
- Fe(II) content in particulate emissions from the air atomization heater was very low.
- Based on the results of the Fe(II) analyses and on the assumption that iron exists primarily in ionic forms in combustion emissions, Fe(III) was determined to be the major Fe species in emissions from the air atomization heater fired with waste oil.

PAH EMISSIONS

- Several PAH compounds were found at elevated levels in gaseous emissions from both residential heaters tested.
- Vaporizing pot emissions had a higher PAH content than the air atomization heater and, based on literature estimates, also higher than residential heaters fired with commercial fuel oil.
- In addition to the potential health hazards associated with PAH and Fe(III) species in combustion emissions, the elevated levels of both of these constituents is cause for even greater

concern since combinations of benzo(a)pyrene and Fe(III) have been shown to promote certain types of mammalian cancer.

ORGANOLEAD COMPOUNDS

- No organolead compounds were detected in emissions from the air atomization heater.
- The sampling and analysis methods developed in this study for determination of volatile organolead emissions should be useful in determinations of other organometallic species in combustion emissions.

FUEL SAMPLES

- Analysis of the double filtered automobile oil sample revealed comparatively lower levels of metallic species indicating that filtration should be an effective pretreatment for reducing metal content in waste oil fuel and subsequently, lowering the associated emissions.
- Comparison of metal content in fuel oil sampled from the top and bottom of storage tanks suggested that sedimentation during storage can slightly reduce certain metals in waste crankcase oil.

SECTION 3

RECOMMENDATIONS FOR FUTURE RESEARCH

The results of this study indicate potential environmental problems associated with waste crankcase oil combustion applications. One problem is the apparent trend toward increasing PAH levels in automotive fuels and in the resultant crankcase oils available as heating fuels. PAH levels in waste oil should be monitored over time to determine if the trend actually is occurring. This work would require a suitable data base that reflects representative sampling techniques and regional supplies of crankcase oil in the United States since vehicle fuels and engine oils are blended differently in various areas of the country.

Another problem associated with waste crankcase oil combustion is the possible exposure to potentially harmful PAH and metallic species which is strongly suggested by the elevated levels detected for these substances in the test emissions. Generalized dispersion models incorporating multiple source terms and indoor air pollution estimates should be developed to measure the impacts from this source in the urban environment. These models should include geographic distribution of waste oil heating appliances and representative waste oil analyses in the localities where the heaters are used. Once complete models of this type have been developed, the health impacts of waste oil-fired residential heating appliances can be accurately assessed.

The fuel analyses performed in this study indicated that filtration can reduce metal content in waste crankcase oil. The same effect is produced to a very minor extent by sedimentation. Obviously, other clean-up strategies should be investigated. Distillation or sorbent bed partitioning, as used in waste oil recycling processes, might provide a fuel that is environmentally more acceptable than raw waste crankcase oil.

SECTION 4

EXPERIMENTAL METHODS AND PROCEDURES

SAMPLING PROCEDURES

Waste oil combustion tests were performed at the U.S. Environmental Protection Agency's Industrial Environmental Research Laboratory at Research Triangle Park, North Carolina. The tests consisted of burning waste fuel oil in the vaporizing pot and air atomization heaters.

A schematic diagram of the test heaters is given in Figure 1. The principal difference in the two systems is in the way the flame is sustained in each heater's firebox. The air atomization unit injects aerosolized oil vapor into the burn chamber and the combustion emissions are discharged as gases and particulates into the flue. By contrast, the vaporizing pot heater operates through volatilization of heated oil. The vapors are burned and a residue is left behind in the vaporizing pot. In the previous study, this residue was found to contain a major portion of the metallic species from the waste crankcase oil.

Waste Oil

The waste oil samples were selected and sampled to provide information on possible preliminary treatment that could be used to avoid or reduce harmful discharges upon combustion. Two physical treatments--sedimentation and filtering--were performed on the waste oils. The sampling locations and history of the oils are listed in Table 1. During the Phase II combustion tests, only automotive waste crankcase oil was fired.

PAH and Particulate Emissions

Emissions generated by the heaters in the tests were sampled with a Modified Method 5 (MM5) train. Two MM5 samples were collected from each heater under the conditions shown in Tables 2 and 3. A schematic diagram of the MM5 sampling train is shown in Figure 2. The MM5 train separates the sample into a particulate fraction in the heated probe and filter section, and a semivolatile organics fraction which collects on the XAD-2 resin. The MM5 samples were analyzed for PAH and selected inorganic compounds.

Organolead Compounds

No standard EPA method for sampling organolead compounds in combustion emissions was available at the time of this study and consequently several techniques were reviewed for applicability. Cryogenic sampling often is used

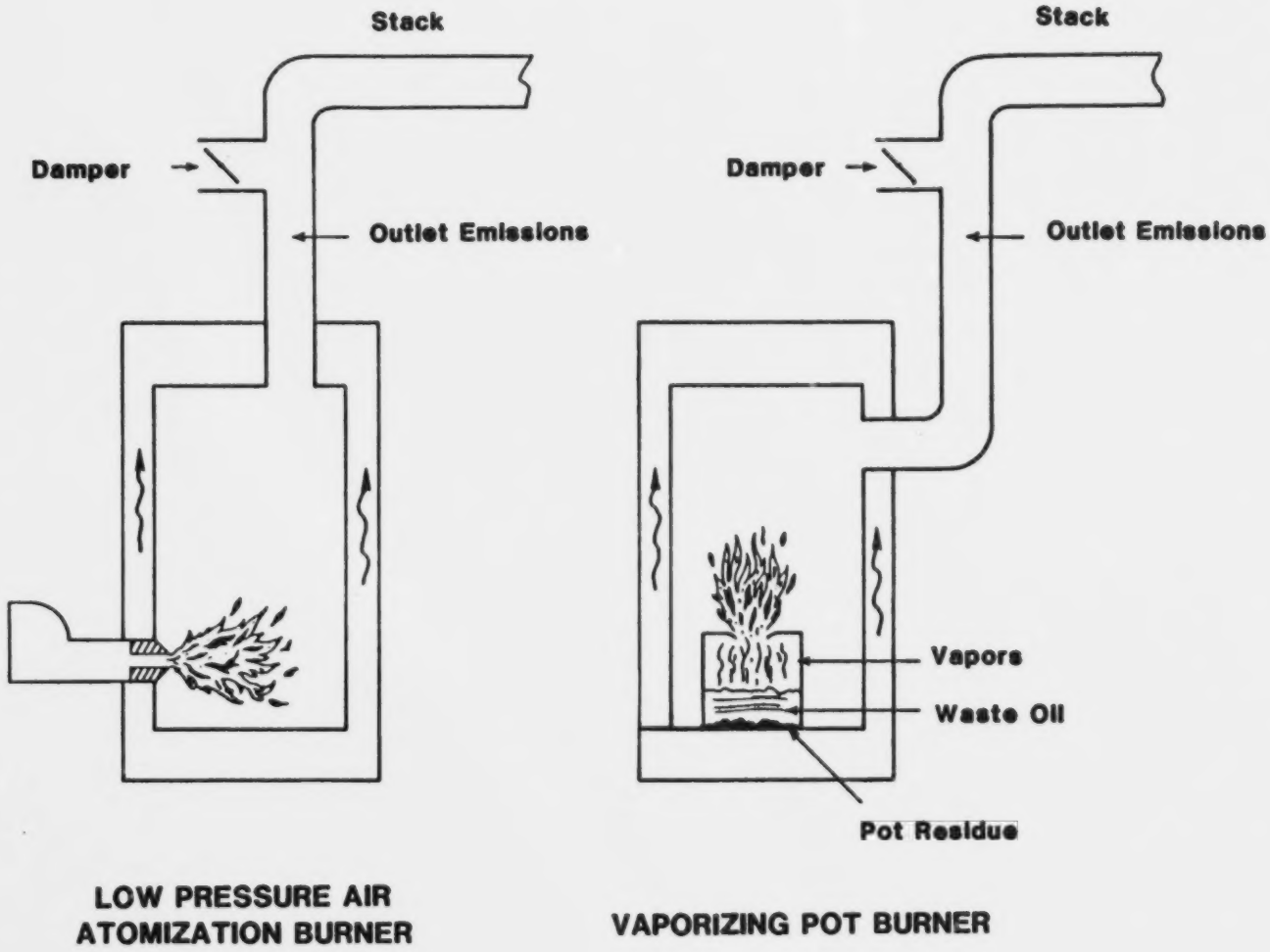

Figure 1. Test combustion systems

TABLE 1. WASTE OIL SAMPLE HISTORY

Sample Designation	Date Collected	Use	Sample Position in Tank
AT	7/20/82	Auto Crankcase	Top
AB	7/20/82	Auto Crankcase	Bottom
TT	7/20/82	Truck Crankcase	Top
TB	7/20/82	Truck Crankcase	Bottom
DF	12/9/82	Auto Crankcase	Double filtered
MST2	10/5/82	Auto Crankcase	Mix from two tanks

TABLE 2. TEST CONDITIONS FOR VAPORIZING POT COMBUSTION EXPERIMENTS

	Run 1		Run 2	
Barometric pressure, MPa (in. Hg)	0.102	(30.2)	0.102	(30.1)
Stack temperature, °C (°F)	411	(711)	419	(786)
Stack velocity, m/sec (ft/sec)	3.7	(12.2)	3.7	(12.2)
Meter temperature, °C (°F)	38	(101)	40	(104)
Isokinetic variation, %	112.7		109.7	
Corrected dry volume, scm (scf)	3.6	(126)	4.0	(143)
Moisture volume, scm (scf)	0.29	(10.4)	0.31	(11.1)
Flue gas composition				
H_2O, %	7.7		7.2	
CO_2, %	7.3		7.0	
O_2, %	11.7		11.8	
CO, ppm (v/v)	10		10	
Calculated molecular weight	28.87		28.87	
Auto crankcase oil used, l (gal)	15	(4)	14	(3.7)
Test time, minutes	280		330	
Rate, l/hr (gal/hr)	3.2	(0.85)	2.5	(0.66)
Pot residue, g	290		310	
Residue deposition rate				
g/cc	0.0193		0.0222	
g/min	1.03		0.94	
Average Δ P @ orifice plate, Pa (in. H_2O)	158	(0.635)	175	(0.703)

TABLE 3. TEST CONDITIONS FOR AIR ATOMIZATION COMBUSTION EXPERIMENTS

	Run 1		Run 2	
Barometric pressure, MPa (in. Hg)	0.102	(30.2)	0.102	(30.1)
Stack temperature, °C (°F)	266	(511)	266	(511)
Velocity, m/sec (ft/sec)	1.4	(4.6)	1.4	(4.6)
Meter temperature, °C (°F)	40	(104)	40	(104)
Isokinetic variation, %	657		361	
Corrected dry volume, scm (scf)	4.3	(151)	3.3	(117)
Moisture volume, scm (scf)	0.40	(14)	0.34	(12)
Flue gas composition				
H_2O, %	8.3		9.3	
CO_2, %	10-11		10-11	
O_2, %	6.8		6.8	
CO, ppm (v/v)	50		50	
Calculated molecular weight	28.36		28.24	
Auto crankcase oil used, l (gal)	22	(5.81)	31	(3.21)
Test time, minutes	220		311	
Rate, l/hr (gal/hr)	7.3	(1.6)	7.3	(1.6)
Average ΔP @ orifice plate, Pa (in. H_2O)	520	(2.1)	92	(0.37)

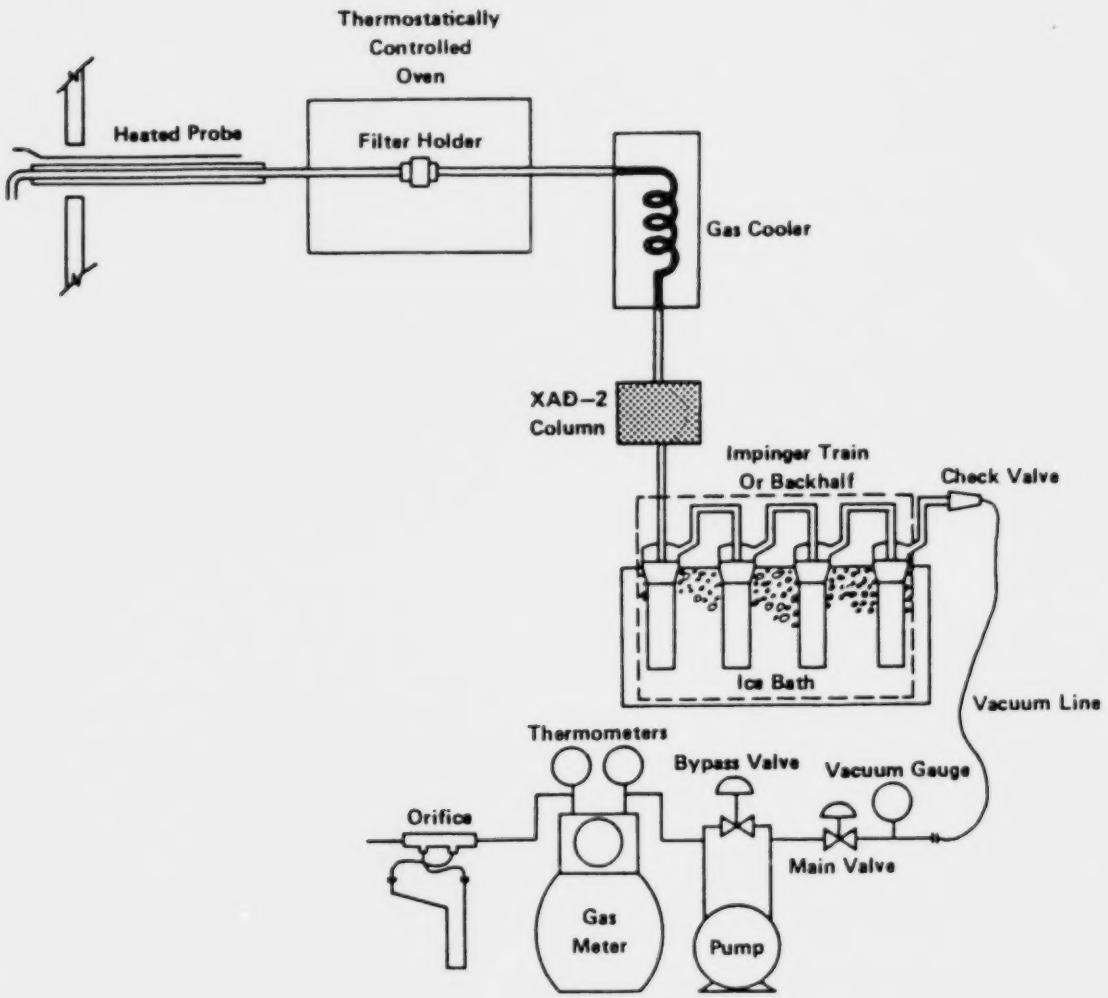

Figure 2. Modified Method 5 sampling train

to collect organolead compounds in source and ambient samples (5). EPA has recently completed preliminary research that indicates resin trapping, XAD-2, may work well to collect these compounds (6). In this program, cryogenic trapping was selected for sampling the organolead compounds because this technique was documented in the literature, and the sample preparation and handling procedures were also developed (7). A special cryogenic sampling train was designed for use with the test heating appliances. A diagram of this system is shown in Figure 3. The train consists of two traps joined with 24/12 ball joints which allow the traps to be demounted easily and capped to seal collected volatile constituents. Since preliminary sampling trials indicated that the water found in combustion gases condenses in the sampling train and can plug the transfer lines, the normal alignment of Trap 1 was reversed and the size of the first tube was increased. The transfer lines are 1.2 cm (0.5 in.)(O.D.) while Tube 1 is 4.5 cm (1.8 in.) (O.D.) and Tube is 2.5 cm (1.0 in.)(O.D.). Two samples were collected with the cryogenic sampling train: one with liquid nitrogen as the cryogenic liquid (Run 1) and the second with carbon dioxide/methanol slurry (Run 2) as the cryogenic liquid. When using liquid nitrogen, the trap had to be warmed periodically to release condensed liquid oxygen.

In preparation for sampling, the train was capped at the probe and pump ends, then allowed to come to the temperature of the cryogen bath. Sampling was initiated by connecting the train to the probe and pump. Emissions were sampled at a flow rate of 250 cc/min for about 4 hours. At the end of the sampling period, the train was capped and stored in the Dewar containing the cryogenic liquid.

Extraction of the samples was performed by washing 5 ml of "distilled-in-glass" isooctane through the probe and adding this liquid extractant to Tube 1, then recapping Tube 1. A separate 5-ml portion of isooctane was added to Tube 2. Still sealed, the two cryogenic sampling tubes were warmed successively from liquid nitrogen to the temperature of the solid carbon dioxide/methanol slurry, then to ice temperature. While at ice temperature, the tubes were shaken for 2 minutes. All surfaces were washed with the extracting solvent. The isooctane extractive rinses were withdrawn from the collection tube with a disposable Pasteur pipette. This process was repeated twice to give a final extraction volume of 15 ml from each tube. The isooctane extracts were sealed in amber vials with Teflon-lined caps for storage and shipping.

ANALYTICAL METHODS

Particulate Emissions

The substances of interest in the analysis of the MM5 particulate filter samples were those species which had been detected in the Phase I study at relatively high levels in waste oil combustion emissions: iodine (I), cadmium (Cd), iron (Fe), zinc (Zn), lead (Pb), chlorine (Cl), and bromine (Br). In addition, during the planning of this study, the possibility of determining anion speciation was considered. Differentiating the various salt forms of inorganic species, e.g., PbO from $PbSO_4$, would be very difficult in this matrix since the Level 1 analysis revealed a complex elemental composition with many

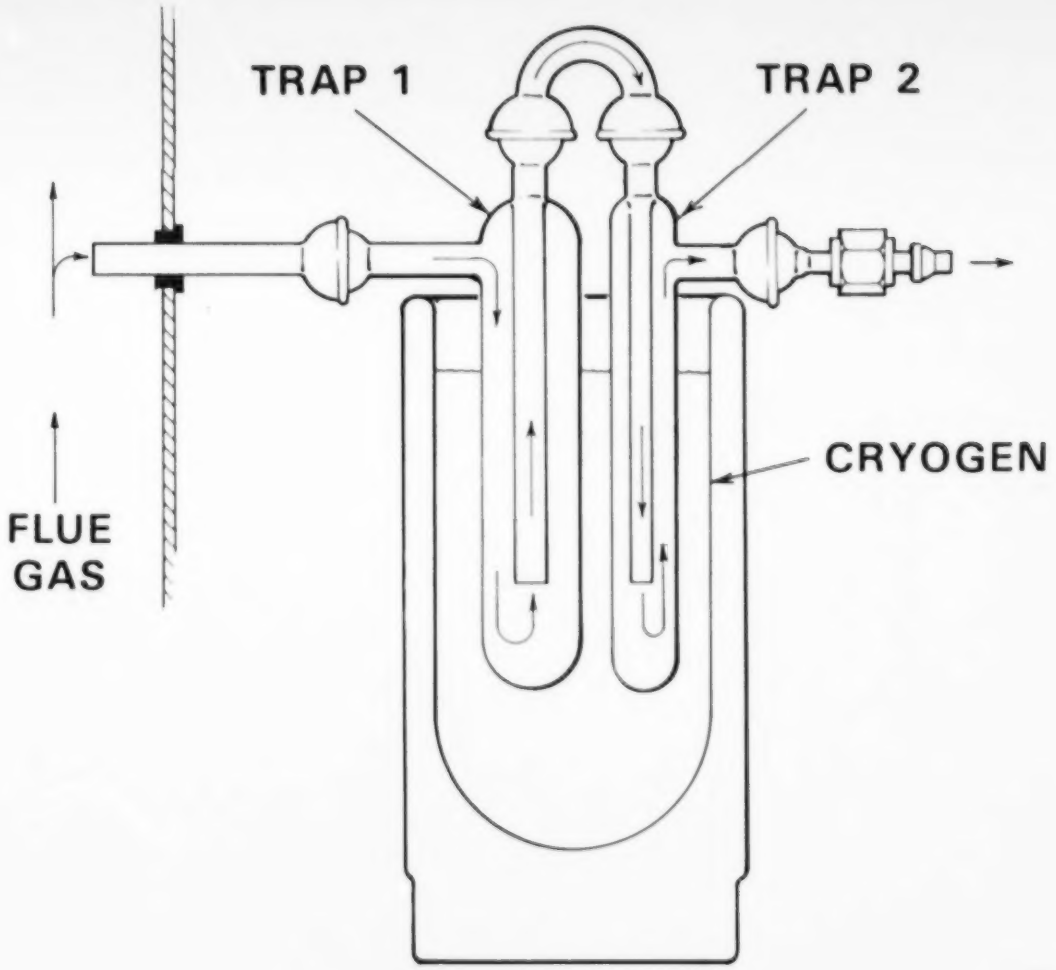

Figure 3. Cryogenic sampling train for collecting volatile organometallic emissions

potential anion species: oxide, chloride, sulfate, sulfite, sulfide, bromide, bromate, etc. However, since iron was identified as one of the predominant metallic elements in waste oil combustion emissions, an attempt was made to identify the relative amounts of the iron species in the particulate emission samples. Consequently, two analyses were conducted on the MM5 particulate samples: X-ray fluorescence analysis of the seven elemental species of interest and a ferrous ion (FE(II)) determination to allow a calculation of the Fe(II)/Fe(III) ratio in the emissions.

X-Ray Fluorescence Analyses

X-ray fluorescence analyses were performed on three MM5 filter catches from the air atomization heater tests. Two of the filter samples, designated #3 and #5, were partial runs with weights of 0.6527 g and 0.5932 g, while the third (#6) represented a complete test run and had a net weight of 0.8719 g. The analyses were conducted with a Kevex Energy Dispersive X-ray Analyzer. This instrument possesses the capability of a computer-controlled fundamental parameter program to obtain quantitative results.

The three particulate samples were analyzed as solid deposits directly on the fiberglass filters. Appropriate circles (3 cm O.D.) were cut to fit the sample tray holder. The samples were irradiated with different target materials to provide enhanced peak sensitivity throughout the elemental range. A dysprosium (Dy) target was used to irradiate the samples for analyses of I, Pb, and Zn. A silver (Ag) target was used for Pb, Br, and Fe, and a titanium (Ti) target was used for Cd and Cl. Spectra were acquired for 200 seconds for all target irradiations. A calibration standard containing the analytes of interest was prepared from oven-dried components which were certified at least 95% purity. The components were weighed, mixed, and pressed into a suitable pellet. The source components and composition of the calibration standard are presented in Table 4.

Ferrous Ion Analysis

The ferrous ion (Fe(II)) content of the three air atomization MM5 filter samples was determined using a bathophenanthroline photometric method. The principle of the method is based on the formation of ferrous bathophenanthroline complex in a solution buffered at pH 5 with subsequent extraction in chloroform. The absorbance of the complex at 533 nm was used to estimate the ferrous ion content from a previously prepared calibration curve. The calibration curve was constructed using ferrous ammonium sulfate as a standard. The filter samples were prepared by weighing the filter and digesting the sample in 50 ml of 5% HCl under a CO_2 atmosphere. The cooled solution was diluted to 100 ml, from which a 20 ml aliquot was treated with the bathophenanthroline reagent.

PAH Emissions

The four MM5 train samples collected in the combustion tests were analyzed for PAH by high resolution gas chromatography mass spectrometry (HRGC/MS). To prepare for this analysis, the XAD-2 resin sample was extracted with methylene chloride, along with the particulate-laden filter, in a Soxhlet

TABLE 4. SOURCE AND COMPOSITION OF SOLID SYNTHETIC STANDARD

Compound	Element	Percent (W/W)
PbO_2	Pb	30.3
$NaSO_4$	S	2.5
KBr	Br	4.5
Fe_2O_3	Fe	4.7
NaI	I	3.8
KCl	Cl	3.2
$CaCO_3$	Ca	1.0
$BaCO_3$	Ba	3.1
ZnO	Zn	1.8
CuO	Cu	1.8
MoO_3	Mo	1.5
CdO	Cd	3.84
--	O	16.4
--	Na	5.8
--	K	5.9
--	C	11.9

extractor. The filter was re-extracted separately with benzene to remove PAH compounds not extracted by methylene chloride. The resin-filter extract was combined with the extracts of the aqueous impinger. This combined sample, which contained most of the organic burden, was analyzed by gas chromatography and gravimetry to determine condensible organics. The combined organics sample and the benzene filter extract were then combined and reduced to about 1 ml with a Kuderna-Danish concentrator, and to a final volume of 0.5 ml by directing a gentle stream of nitrogen across the top of the sample. An internal standard was spiked into the sample at this point.

The GC/MS system used for the PAH analyses consisted of a Finnigan Model 9500 biomedical type gas chromatograph coupled with a Finnigan Model 3200 mass spectrometer. Data collection and processing were handled by a Finnigan INCOS Data System which utilizes a Data General Nova 3 computer with 32K memory. A 30 m SE-54 capillary column was coupled directly to the mass spectrometer via a quartz capillary transfer line. The gas chromatograph was equipped with a Grob-type injector for on-column injection. The column was temperature programmed from 160-320°C at 4°C/min. Injector temperature was 300°C while the GC/MS transfer line was held at 315°C.

The separation efficiency and high temperature stability of HRGC/MS is shown in Figure 4 for a standard mixture of PAH compounds. Compounds such as coronene and dibenzopyrenes with boiling points above 520°C are eluted as sharp peaks. Close-to-baseline separation is achieved for isomeric compounds such as phenanthrene/anthracene, benzo(a)anthracene/chrysene and benzo(a)-pyrene/benzo(e)pyrene.

Organolead Compounds

As with the sampling system for organolead compounds, an analytical method had to be developed for the determination of these compounds. Lead alkyls are a common fuel additive, used as an antiknocking ingredient in gasoline. The principal species used commercially are the methyl and ethyl substituents, predominantly tetramethyl (TML), trimethylethyl (TMEL), dimethyldiethyl (DMDEL), methyltriethyl(MTL), and tetraethyl (TEL) lead.

The method most commonly used to measure alkyl lead compounds is gas chromatography (GC) coupled to an atomic absorption spectrometer (AAS) (8). The AAS acts as a sensitive detector for lead. Radziuk et al. used cryogenic sampling and GC/AAS to measure ambient alkyl lead with a graphite furnace technique to demonstrate instrument sensitivity of 40 pg Pb, which corresponded to about 0.5 ng/m^3 in a 70 L air sample (5). After experimenting with the GC/AAS interfaces proposed in the literature, a modification was used in this study which greatly improved instrument sensitivity for direct flame atomization. This modified interface consisted of a 0.3 cm (1/8 in.) (O.D.), stainless steel GC tube mounted directly into the base of the AAS burner and attached to the GC column. The effluent from the GC column is passed through this tube and the entire effluent uniformly aspirated across the flame front. A diagram of this interface is shown in Figure 5.

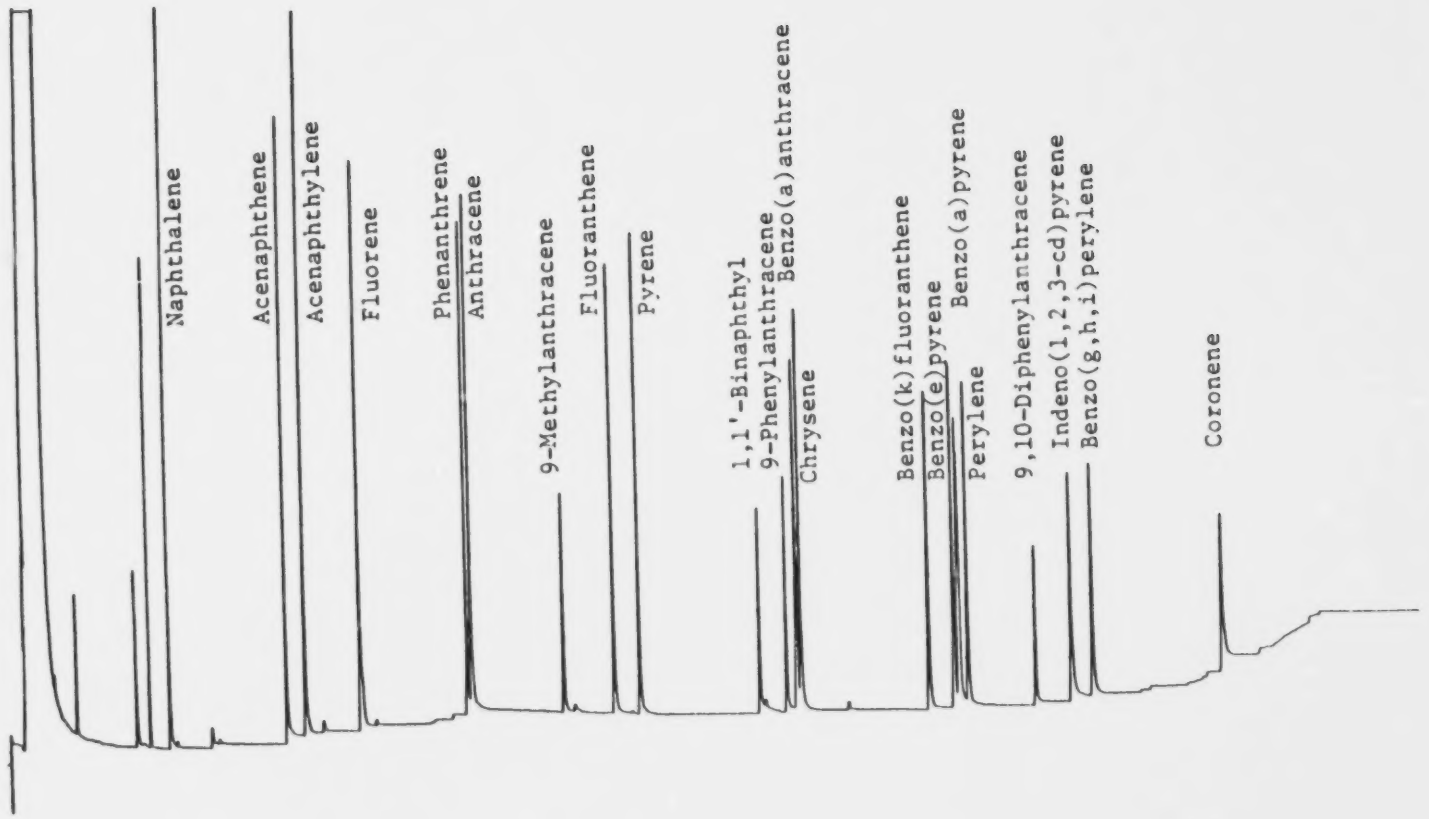

Figure 4. Gas chromatogram of PAH standard mixture

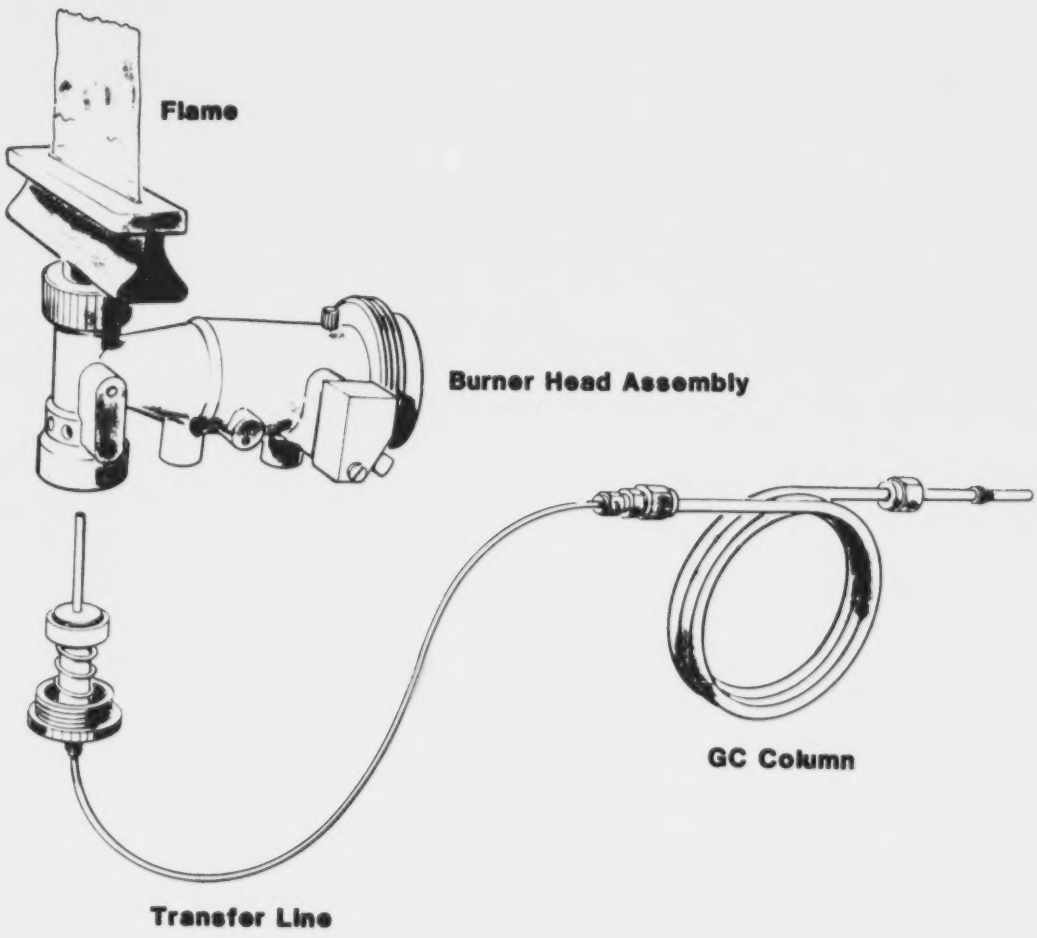

Figure 5. Gas chromatograph interface to the atomic absorption spectrometer burner head

The GC/AAS system used was a Varian Model 1400 GC interfaced as shown to a Perkin Elmer Model 5000 AAS. The GC was equipped with a 0.9 m (3 ft) x 0.64 cm (0.25 in.) (O.D.) stainless steel column packed with 10% (W/W) Carbowax 20M on 100/150 mesh Porasil C. The column was held isothermal at 130°C and helium (120 ml/min) was the carrier gas. The reference standard used for calibration was provided by the Ethyl Corporation (MLA-500(T313)) and contained 1.53 mg Pb per ml of solution in isooctane. The concentrations, retention times, and estimated detection limits for the individual tetraalkyl lead species in the reference mixture are given in Table 5.

TABLE 5. ALKYL LEAD REFERENCE MIXTURE - MLA-500(T313)

Compound	Concentration	Retention Time	Detection Limit
TML	114 µg/ml	0.61 min	11 ng
TMEL	336	0.78	22
DMDEL	548	1.17	30
MTEL	408	1.78	47
TEL	123	3.00	81

Chromatograms showing the separation and rapid elution (<4 min.) capabilities of the GC/AAS system are shown in Figure 6. The upper chromatogram shows a 50 µl injection representing 5.7-27.4 µg of the alkyl lead compounds. The lower chromatogram shows a 5 µl injection representing 0.6-2.7 µg of each compound. At high sample loading on the GC column, as shown in the upper chromatogram, TML and TMEL show overlap and loss of resolution. Resolution is restored by reducing the amount of sample analyzed.

Waste Oils

The six waste oil samples were analyzed by X-ray fluorescence to determine baseline amounts of the elemental species of interest in the particulate emissions and to assess the effect of filtration and sedimentation processes on metal content in the fuels. The samples were thoroughly mixed and positioned in plastic cups containing a thin ($\sim$ 4 µm) Mylar window. The Kevex Energy Dispersion X-ray analyzer was used for these analyses. A dyprosium (Dy) target was used to irradiate samples for analyses of I, Cd, Pb, and Br. A germanium (Ge) target was used for Zn, Fe, and Cl analyses. The acquisition

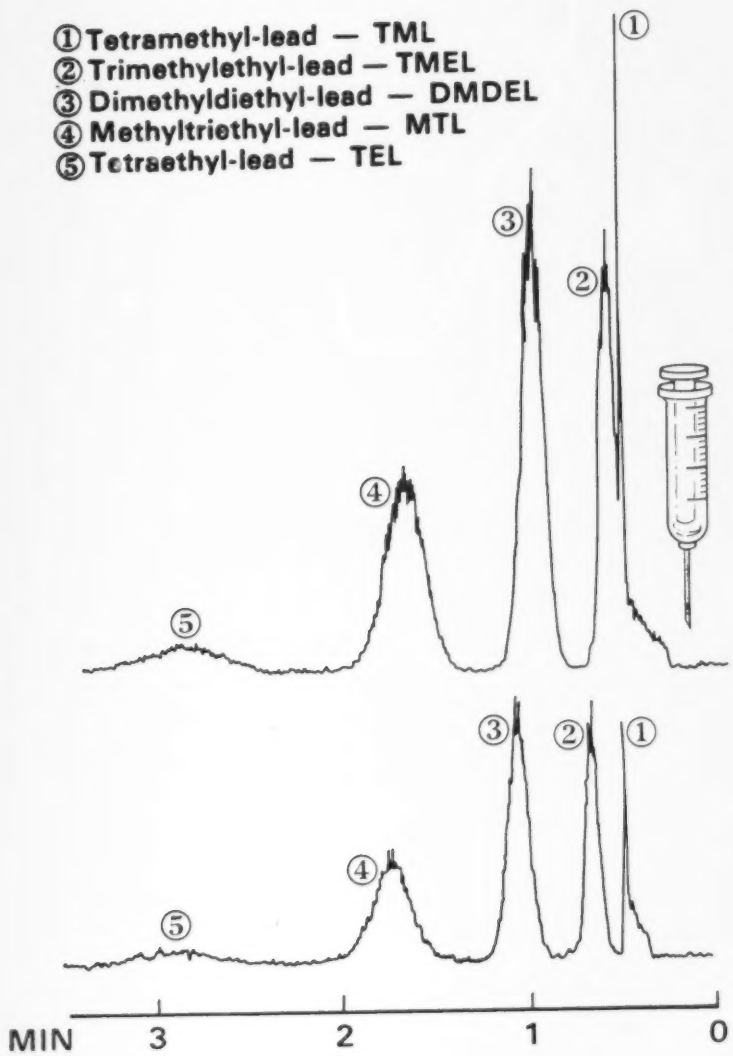

Figure 6. Chromatograms of tetralkyl lead compounds in the GC/AAS system

time for oils was 500 seconds. The calibration standard used for these analyses was prepared from organometallic reference compounds and halogenated hydrocarbons. The base matrix used for the standard was pure distillate oil. The compounds used, and the analyte and matrix elements present in the standard, are shown in Table 6.

TABLE 6. SYNTHETIC STANDARD FOR WASTE OILS

Compound	Element	Percent (W/W)
1-Chloro-6-hydroxyhexane	Cl	1.2
2-Bromoethylbenzene	Br	2.6
Iodobenzene	I	2.4
Pb naphthenate	Pb	3.4
Cd octoate	Cd	0.89
Fe naphthenate	Fe	0.44
Zn octoate	Zn	0.51
S octoate	S	0.31
	C	78.5
	H	8.7
	O	0.5

SECTION 5

RESULTS AND DISCUSSION

WASTE OILS

The results of the X-ray fluorescence analysis of the six waste oil samples are shown in Table 7. The amounts of the elements analyzed are listed as weight percent and as grams per gallon. The latter value is based on an estimated density of 0.8 g/ml for the waste oils burned. The Cl values listed in Table 7 were confirmed with a wavelength specific X-ray fluorescence procedure.

The data in Table 9 show that essentially no concentration gradient exists for Pb, Br, and Zn between top and bottom positions for stored waste oils. The doubled filtered oil sample (DF) has a pronounced reduction in the levels of Zn and Fe due to filtering. These observations are graphically illustrated in the X-ray fluorescence spectra of the automobile, truck and double filtered oil samples presented in Figures 7 through 11. The vertical scale (instrument response) in the truck oil spectra is 50% of the vertical scale in the automobile oil spectra. The target peak is used to provide normalization of the elemental peaks in these spectra. Additional X-ray fluorescence spectra of the oil samples are presented in Appendix A. These spectra include the six spectra obtained from analyses with the Ge excitation target and the MST2 spectrum obtained with the Dy target.

The current study was partially intended to determine what handling techniques could be used to reduce toxic emissions during the combustion of waste oils. Two handling techniques were investigated in this program. One technique was the effect of sedimentation measured by sampling from the top and bottom of oil tanks which were not disturbed for 46 weeks. As previously described, automotive fuel oil data (AT and AB) of Table 9 indicate that essentially the same concentration of Pb, Br, and Zn was obtained for the bottom and top sample. This result indicates that the process of sedimentation has no effect on removal of these metals.

Some insight as to how these metals are present in the oils may be offered. As stated earlier, all oil samples were shaken vigorously prior to loading into the cups for analysis. In the automobile samples, AT, AB, and MST2, a bottom deposit was visible in the original sample bottle. This deposit could not be re-entrained in the oil even by scraping. No visible deposits were noticed in the TT, TB, and DF oil samples. The XRF technique can partially discriminate between a well-mixed, uniform sample and a sediment layer. The sample cup used for analysis is irradiated through a Mylar window

TABLE 7. RESULTS OF X-RAY FLUORESCENCE ANALYSIS OF WASTE OILS

Waste Oil Sample	Unit	Element						
		I	Cd	Pb	Br	Zn	Fe	Cl
Automobile Top Position (AT)	Weight %	<0.01	< 0.01	1.2	0.41	0.3	0.05	0.17
	grams/gal*	<0.3	<0.3	41	14	10	2	6
Automobile Bottom Position (AB)	Weight %	<0.01	< 0.01	0.85	0.29	0.25	0.05	0.17
	gram/gal	<0.3	<0.3	30	10	9	2	6
Truck Top Position (TT)	Weight %	<0.01	< 0.01	0.04	0.005	0.15	0.015	0.05
	gram/gal	<0.3	< 0.3	1	0.2	5	0.5	2
Truck Bottom Position (TB)	Weight %	<0.01	< 0.01	0.045	0.006	0.15	0.015	0.06
	gram/gal	<0.3	<0.3	2	0.2	5	0.5	2
Automobile Double Filtered (DF)	Weight %	<0.01	< 0.01	1.15	0.3	0.001	0.001	0.15
	gram/gal	<0.3	< 0.3	39	10	0.03	0.03	5
Automobile (MST 2)**	Weight %	<0.01	<0.01	1.3	0.44	0.3	0.05	0.2
	gram/gal	<0.3	< 0.3	44	15	10	2	7

* Based cn assumed densities of 0.895 g/ml.
** Baseline value for fuel used in air atomization test runs.

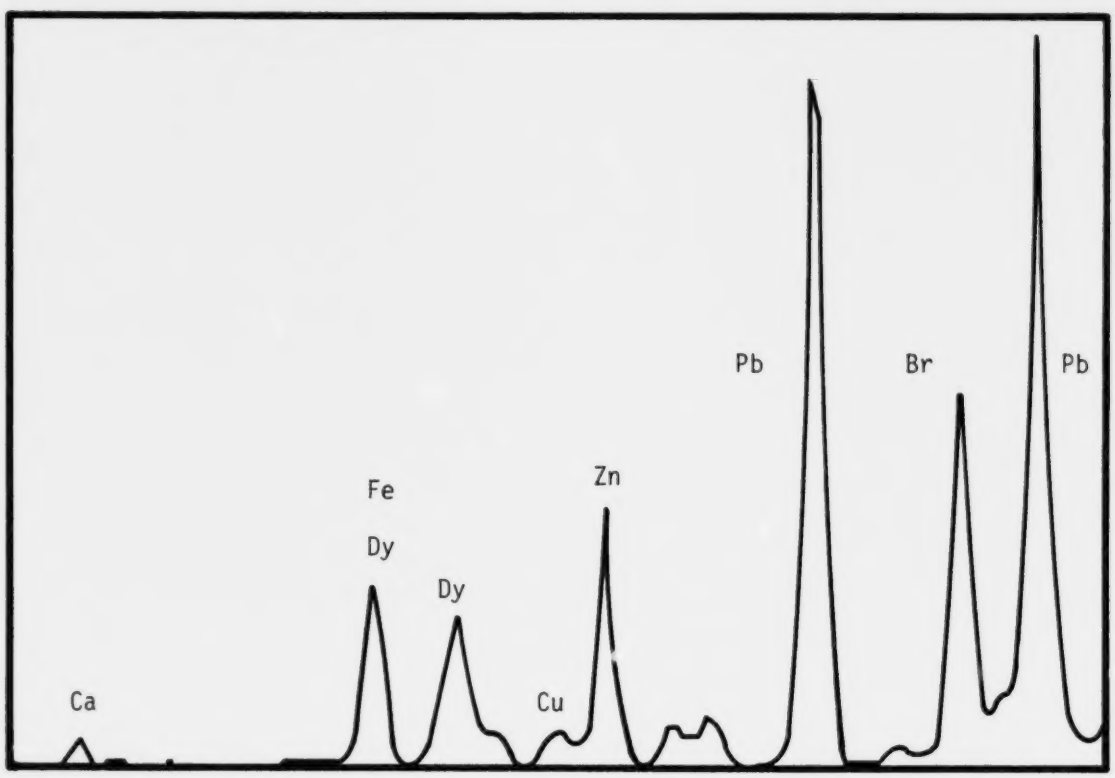

Figure 7. Spectrum of automobile oil samples (AT) using Dy target

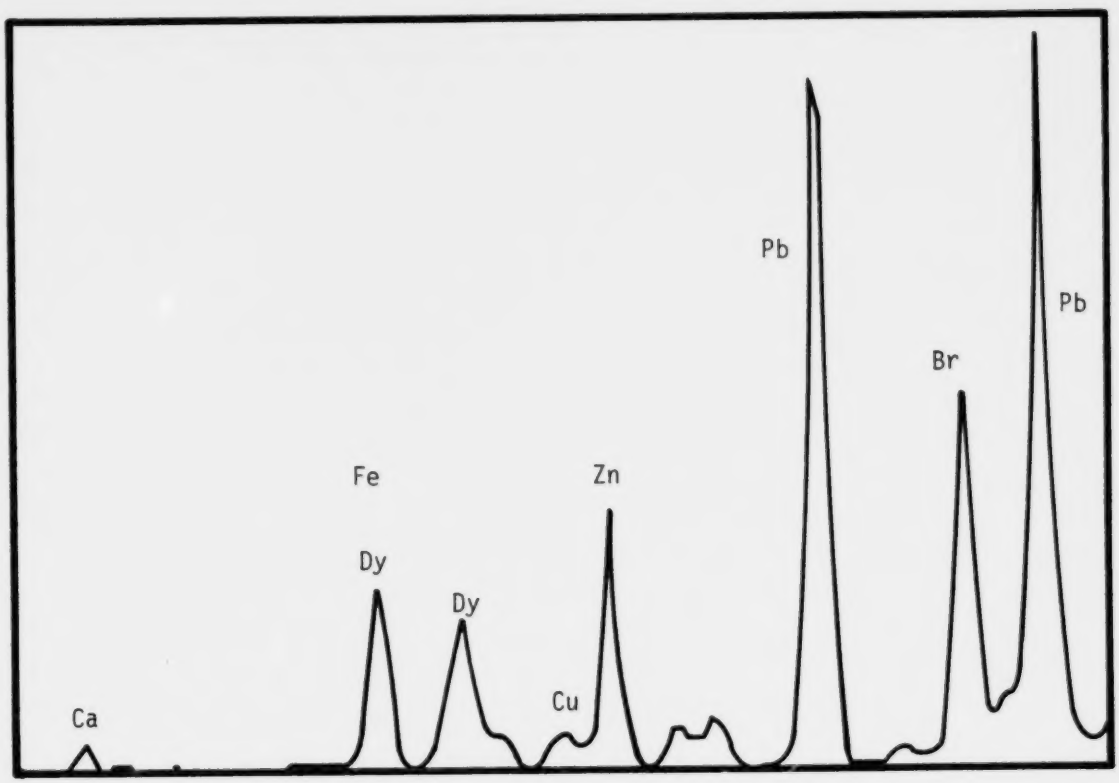

Figure 8. Spectrum of automobile waste oil sample (AB) using Dy target.

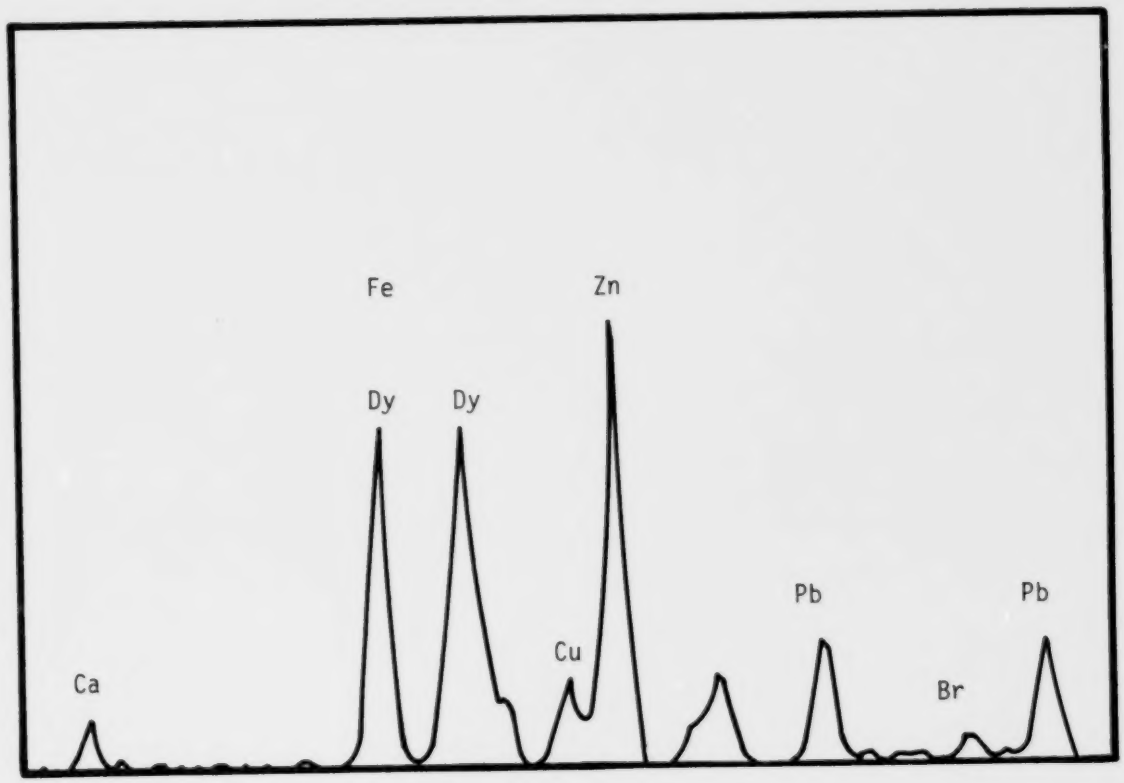

Figure 9. Spectrum of truck waste oil sample (TT) using Dy target.

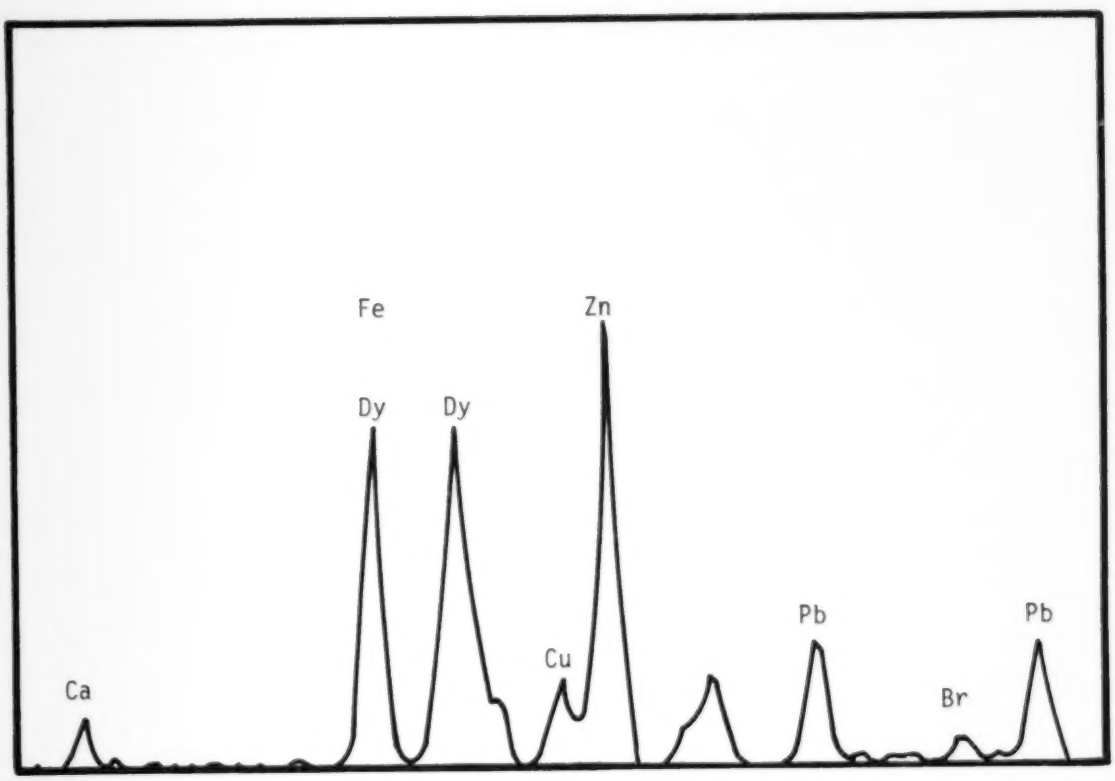

Figure 10. Spectrum of truck waste oil sample (TB) using Dy target.

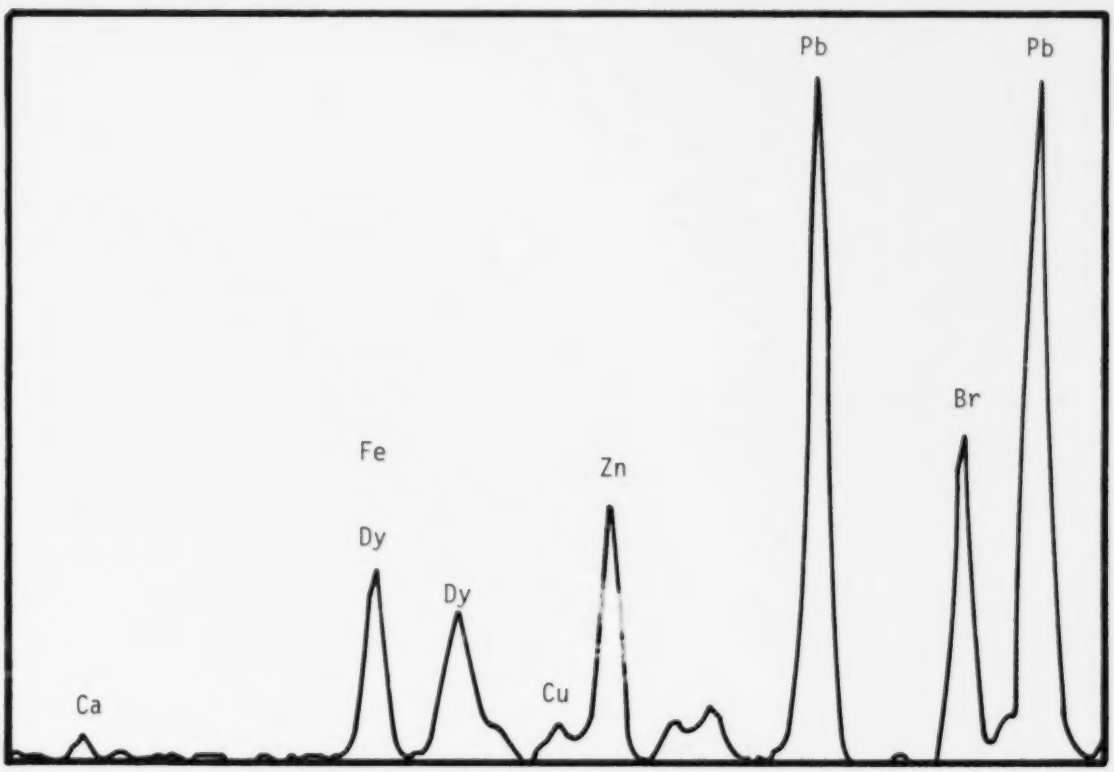

Figure 11. Spectrum of automobile waste oil sample (DF) using Dy target.

in the bottom of the cup. Since the X-ray penetration decreases as a function of depth into the oil layer, the bottom layer is preferentially analyzed over the bulk liquid. Thus, reanalyzing the sample after sedimentation occurred gave a qualitative indication that some species (Fe, Zn, Cl) were concentrating in the sediment layer, while others (Pb, Br) were not. The second examination revealed that the Cl counts more than doubled the initial counts obtained from well mixed samples of AT, AB, DF, and MST2. Additionally, comparison of the two spectra showed the Fe and Zn levels increased and Pb and Br levels remained constant for the waste oils after sedimentation. This result may indicate that sampling had reentrained the separated metal species. It should also be pointed out that uniformity of Pb distribution may indicate that filtration will have only a limited benefit in reducing Pb levels in waste oil fuel.

The results of the double filtered (DF) oil sample analysis indicate that particles associated with Fe and Zn are large enough to be filtered. The Pb and Br appear to be well dispersed and are too small to be filtered or to settle.

From the results of waste oil X-ray fluorescence analyses, filtration was observed to have a positive effect on reducing metallic constituents in waste crankcase oil used for space heating. Results of sedimentation tests were not conclusive and did not support the practice of pumping waste oil from the top of storage tanks, and not from the bottom, to reduce metal emissions. Both Pb and Br, common antiknocking additives in waste oil combustion systems, were found to constitute about 1 percent and 0.5 percent (W/W), respectively, of the automotive waste oil used in these tests.

PARTICULATE EMISSIONS

Elemental Analyses

The results of the X-ray fluorescence analyses of the MM5 particulate emission samples from the air atomization heater (#3, #5, and #6) are given in Table 8. The amounts of the elements analyzed are reported in weight percent of total collection, total weight per catch, and by flue gas concentration. Typical X-ray fluorescence spectra obtained from the particulate samples are shown in Figures 12 and 13 for sample #3. The spectrum in Figure 12 was acquired with a Dy target used for determining heavy elements. The spectrum shown in Figure 13 was acquired using the Fe target and shows higher efficiency in exciting the lighter elements including Mn and Cr. The corresponding spectra for samples #5 and #6 are included in Appendix B, Figures B-1 to B-4.

As previously described, all three of these particulate samples were generated by the combustion of the same automotive waste oil fuel. Therefore, little difference in the elemental content of the samples is seen. These results do confirm the results found in the previous study of waste oil combustion using SASS train and dilution tunnel sampling with spark source mass spectrometry (SSMS) and inductively coupled argon plasma spectrometry (ICAP) analyses (1-2). The data of this study provide an

TABLE 8. RESULTS OF X-RAY FLUORESCENCE ANALYSIS OF PARTICULATES

Sample	Element						
	I	Cd	Pb	Br	Zn	Fe	Cl
Sample #3(1)							
W%	0.01*	0.06	28.6	2.5	8.0	1.82	0.98
Total milligrams	0.07	0.4	187.	16.3	52.2	11.9	6.4
mg/m^3	0.03	0.17	81.	7.1	23.	5.2	2.8
Sample #5(2)							
W%	0.01*	0.06	20.	1.94	6.3	1.54	0.96
Total milligrams	0.06	0.36	118.6	11.5	37.4	9.1	5.7
mg/m^3	0.03	0.18	60.	5.8	19.	4.6	2.9
Sample #6(3)							
W%	0.01*	0.05	29.4	3.4	9.3	2.2	1.0
Total milligrams	0.09	0.44	256.3	29.6	81.0	19.2	8.7
mg/m^3	0.03	0.13	78.	9.0	25.	5.8	2.6

* Not detected, detection limit 0.01%.

(1) 54% of MST 1.
(2) 46% of MST 1.
(3) 100% of MST 2.

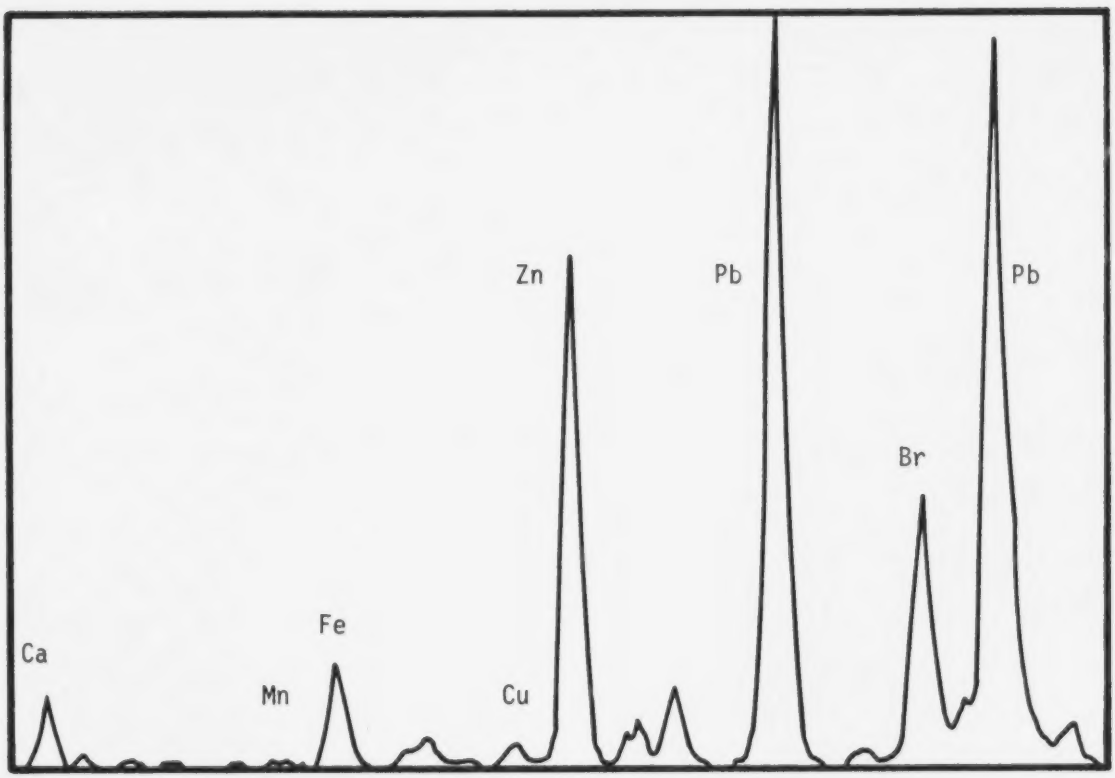

Figure 12. Spectrum for particulate sample #3 obtained with a Dy target.

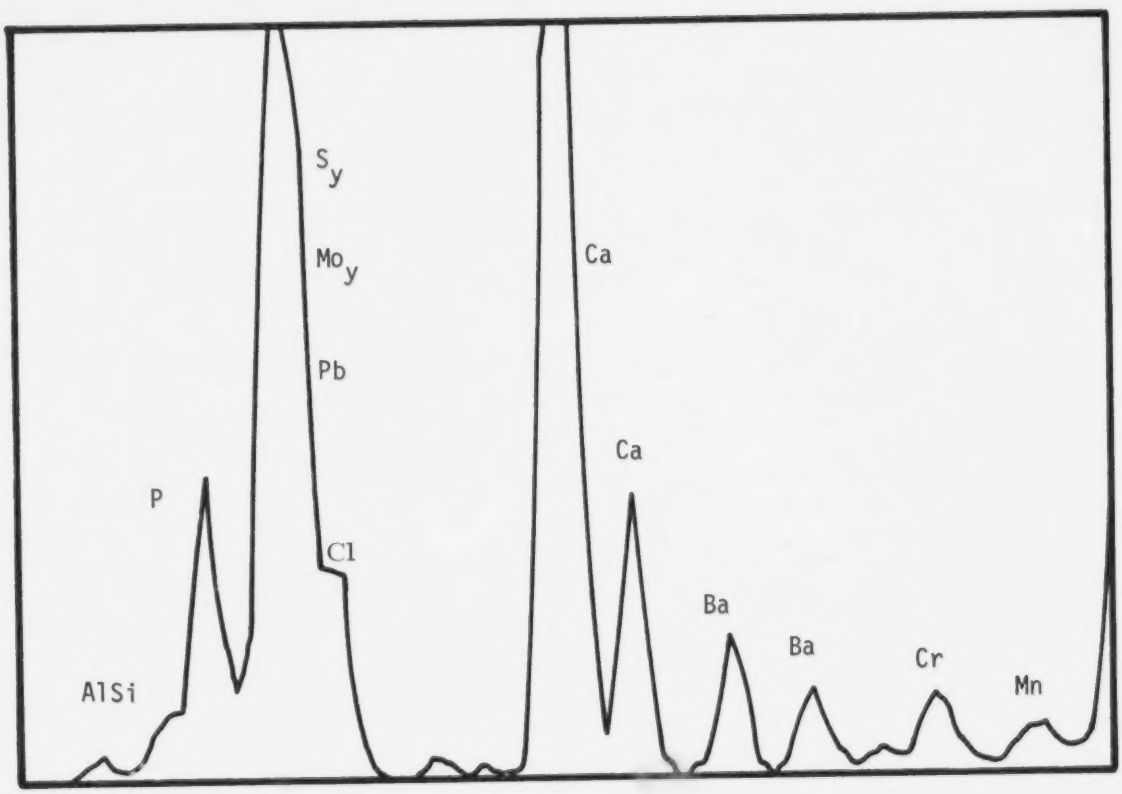

Figure 13. Spectrum for particulate sample #3 obtained with a Fe target.

independent confirmation of elevated metal discharges from the air atomization combustion system. Bromine had only been measured by SSMS in the previous study and this program allowed the opportunity to compare discharge levels of Br. Bromine was found in the particulate emission samples from the air atomization heater at concentrations roughly equivalent to observed iron levels (6-9 mg/m^3) and at concentrations approximately three times higher than gaseous chlorine concentrations observed in air atomizer discharges.

Ferrous Ion Analyses

The results of the analysis of the ferrous ion (Fe-(II)) content in the MM5 particulate samples from the air atomization heater are given in Table 9.

TABLE 9. FERROUS ION CONTENT OF FILTER SAMPLES

Sample	Total Filter Weight (g)	Fe(II) Content		Total* Fe Content (µg)
		Total (µg)	µg/g (ppm)	
#3	0.6527	62	95	11,900
#5	0.5932	52	88	9,100
#6	0.8719	74	85	19,200

* As determined by X-ray fluorescence.

These data indicate that Fe(II) is present at relatively insignificant levels in emissions from the air atomization heater fueled with automotive waste oil. Comparison of Fe(II) data with the X-ray fluorescence results for total Fe content shows that Fe(II) constitutes only a minor portion of the Fe content in these emissions. Since iron is expected to be converted primarily to ionic forms in combustion processes, an assumption can be made that only a relatively small amount of iron will be in the elemental state. Consequently, the amount of Fe(III) in the sample can be estimated by subtracting the Fe(II) content from the total Fe content. The resulting values for Fe(II) are relatively large and the Fe(II)/Fe(III) ratios would. therefore, be small. The predominant form of Fe in the waste oil combustion emissions is, therefore, Fe(III).

PAH Emissions

The results of polynuclear aromatic hydrocarbon analyses are presented in Table 10. In general, the vaporizing pot samples showed higher concen-

TABLE 10. RESULTS OF PAH ANALYSES

Compound	Amount Detected ($\mu g/m^3$ dry)			
	VP-Run 1*	VP-Run 2*	AA-Run 1*	AA-Run 2*
Naphthalene	12	6	5	4
Acenaphthene	--	--	0.3	0.2
Acenaphthylene	2	--	--	--
Fluorene	6	0.6	0.8	0.7
Phenanthrene	70**	5	6	4
Anthracene	--	2	0.2	0.2
Fluoranthene	--	--	0.4	0.5
Pyrene	3	2	0.5	0.5
Benzo(a)anthracene	--	4	0.2	0.4
Chrysene	--	--	0.2	0.4
Benzo(k/b)fluoranthene	--	6	--	--
Benzo(e)pyrene	5	6	--	0.05
Benzo(a)pyrene	6	8	--	1
Perylene	--	6	--	0.6
Indeno(1,2,3-c d)pyrene	--	--	--	0.8
Benzo(g h i)perylene	--	--	0.1	0.6
Anthanthrene	--	--	0.1	1.1
Coronene	--	--	--	0.1

* VP = Vaporizing Pot Sample
AA = Air Atomization Heater Sample
** This apparent high result was verified by fragment ion patterns and appears to be an outlier.

trations of individual PAH species than the air atomization samples. Since Runs 1 and 2 were intended to be duplicates, and were very similar in test conditions and sampling parameters, the observed test-to-test differences reflect the variability of these data.

The data in Table 10 are corrected for a system blank analysis, but are not corrected for method recoveries. Method losses were estimated by the technique of labeled isotope addition. In this method, a known amount of an atomic isotope of the compounds analyzed is spiked into the MM5 train after sampling. The labeled recovery standard used in this analysis was benzo(a)-pyrene-d_{12}, These spikes were administered by liquid injection of 40 µg BaP-d_{12} in benzene solution onto the XAD-2 resin. Quantitative (approximately 100%) recoveries were found for the BaP-d_{12} spikes.

The complexity of the waste oil combustion discharges is illustrated by the total ion chromatogram of the first vaporizing pot MM5 sample given in Figure 14. Obviously, many organic species are present in this sample and the PAH analysis only characterized a few compounds. A total ion chromatogram from the air atomization sample is shown in Figure 15. This chromatogram represents a simpler peak pattern where extracted ion chromatography is used to improve analytical sensitivity.

PAH emissions are of concern since several members of this class of organic compounds are considered to be mammalian carcinogens. One of the oldest tests for PAH carcinogenicity involves skin painting on test animals; thus crankcase oil, which is found to contain PAH, poses a special occupational hazard to mechanics or other workers exposed to crankcase oil on their hands (9).

Many liquid combustion fuels (gasoline, diesel fuel, No. 2 fuel oil) have elevated PAH levels. Fuel and emission PAH levels for several stationary and mobile combustion sources are compared in Table 11. This comparison is made by using a single compound as an indicator molecule. The compound selected is benzo(a)pyrene, which is probably the most extensively studied PAH compound due to the early identification of this substance as an animal carcinogen. From the data in Table 11, it is apparent that many liquid fuels have high inherent BaP levels if discharges and fuels are compared on a weight-of-fuel-consumed basis. The waste oil heaters discharge higher BaP levels than all of the sources compared in Table 7, including equivalent space heaters using No. 2 fuel oil. The removal of lead antiknocking additives from automotive fuel poses a dilemma to the environmentalist. Lead is commonly replaced with aromatic constituents which result in fuels with aromatic content as high as 50-70%, such as found in Europe (12). While ambient lead levels are diminishing, and concurrently the hazard of gasoline antiknocking additives entering residential combustion sources via waste crankcase oil is also alleviated, the high aromatic content of unleaded fuel may actually increase PAH levels. PAH levels are also rising with the increased use of diesel-powered vehicles in the United States. This trend could affect ambient air quality. One researcher estimates that mobile sources currently contribute about 20% of the U.S. ambient burden of PAH (13). Since waste oil heaters are stationary sources, the impact of these combustion systems is localized and can be estimated from dispersion and source apportionment models that include local climatology and

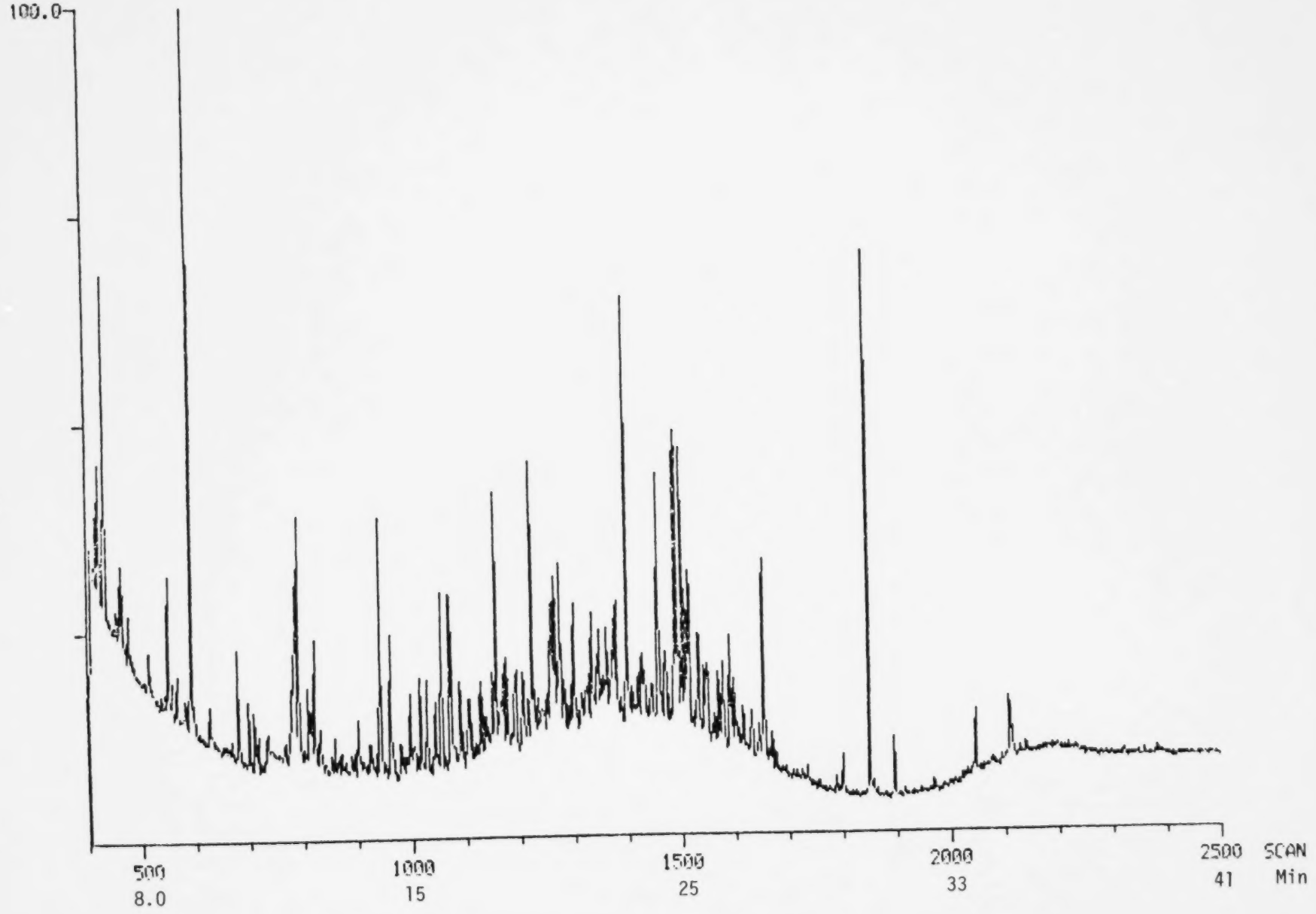

Figure 14. HRGC/MS total ion chromatogram of vaporizing pot sample.

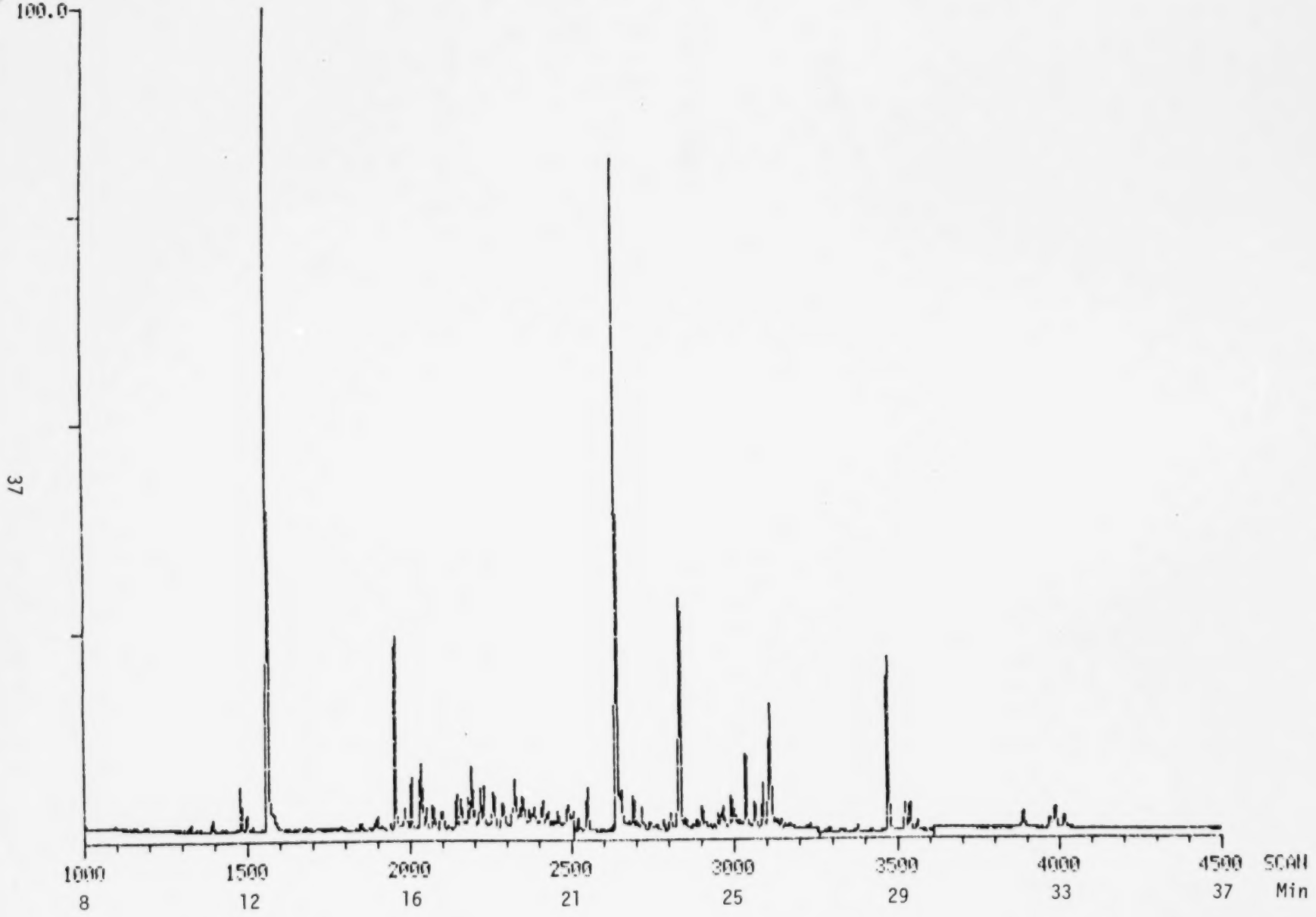

Figure 15. HRGC/MS chromatogram of air atomization emission sample.

TABLE 11. COMPARISON OF BENZO(a)PYRENE CONCENTRATIONS REPORTED IN RAW FUELS AND COMBUSTION EMISSIONS

	Fuel[10] ppm (W/W)	Combustion Emissions ppb (W/W)
Mobile Sources		
Car - Gasoline (catalyst)	0.9 - 9	0.4[11]
Car - Gasoline (no catalyst)	0.9 - 9	5.0[11]
Diesel Engine	1	10.0[11]
Stationary Sources		
Coal-Fire Power Plants	--	0.5 - 3.5[13]
No. 2 Oil - Fire Power Plants	0.01 - 0.05	0.3 - 2.0[13]
No. 2 Oil - Fired Residential Heater	0.01 - 0.05	0.1[11]
Waste Oil - Fire Residential Heaters		
Vaporizing Pot	4 -17[14]	550
Air Atomizer	4 -17[14]	13

(10) Guerin (1978).
(11) Grimmer (1979).
(13) Ramdahl, et al. (1983 - in press)
(14) Becker (1980)

all other PAH sources that contribute to exposure levels for receptors, primarily homes, located nearby a waste oil combustion source.

In addition to potential problems posed by increased PAH levels in fuels and emissions, a serious health hazard is also presented by the combination of benzo(a)pyrene and Fe(III) in combustion emissions. As shown in the previous section, the predominant form of iron in waste oil emissions is Fe(III). Lung cancer has been shown to be elevated in Hematite miners (15,16). Following this discovery, several researchers found that administration of iron oxide (Fe_2O_3) to the respiratory tract of hamsters by intratracheal instillation, together with benzo(a)pyrene, resulted in an increased yield of tumors, while tumors were not found with ferric oxide alone (17-19). The presence of elevated levels of both Fe(III) oxide and benzo(a)pyrene in these samples indicates that the tumorigenic potential of this matrix should receive further study. While the potential for lead emissions will decrease as lead antiknocking agents are removed from U.S. gasoline supplies, iron (III), an engine wear material, will continue as a major contaminant of used engine oil. If the combination of BaP-Fe(III) is carcinogenic in these emissions, this hazard will persist when crankcase oil is used in space heating applications, especially when used in the air atomization heaters. A recent literature report detailed the mutagenicity of waste crankcase oil (20). Based on related studies, waste crankcase oil has been proposed as a listed hazardous waste under the Resource Conservation and Recovery Act, with specific hazards indicated for skin exposure (21). The Level 2 waste oil combustion study revealed that residential heating appliances, fueled with waste oil, discharge many of the harmful species found in the fuel itself into the atmosphere, causing concern as to the environmental safety of these devices.

ORGANOLEAD COMPOUNDS

Analysis of cryogenic samples from the air atomization burner tests indicated that no organolead compounds were present in the emissions. Since alkyl lead species are most likely not formed in the combustion conditions found in burning waste crankcase oil in the air atomizer combustor, the presence of these compounds would be an indication of unburned organolead additives in the waste oil fuel. To determine if organolead compounds were present in the crankcase oil used to fuel the air atomization burner, the waste oil was analyzed directly with the GC/AAS system and produced no measurable alkyl lead signal. The fuel oil then was spiked with a known addition of the Ethyl Reference Standard and analyzed by direct injection onto the GC/AAS analytical system. The chromatogram from that analysis is given in Figure 16. This chromatogram shows measurable peaks (except for TEL) near the detection limit.

If organolead compounds were present in the fuel, they would be at extremely low levels. From the GC/AAS method detection limits cited earlier, this method should measure approximately 20 μg TML/m^3 in flue gas emissions and about 25 mg TML/l in the waste oil fuel. From the previous Level 1 analysis of air atomization burners using the same automobile crankcase oil

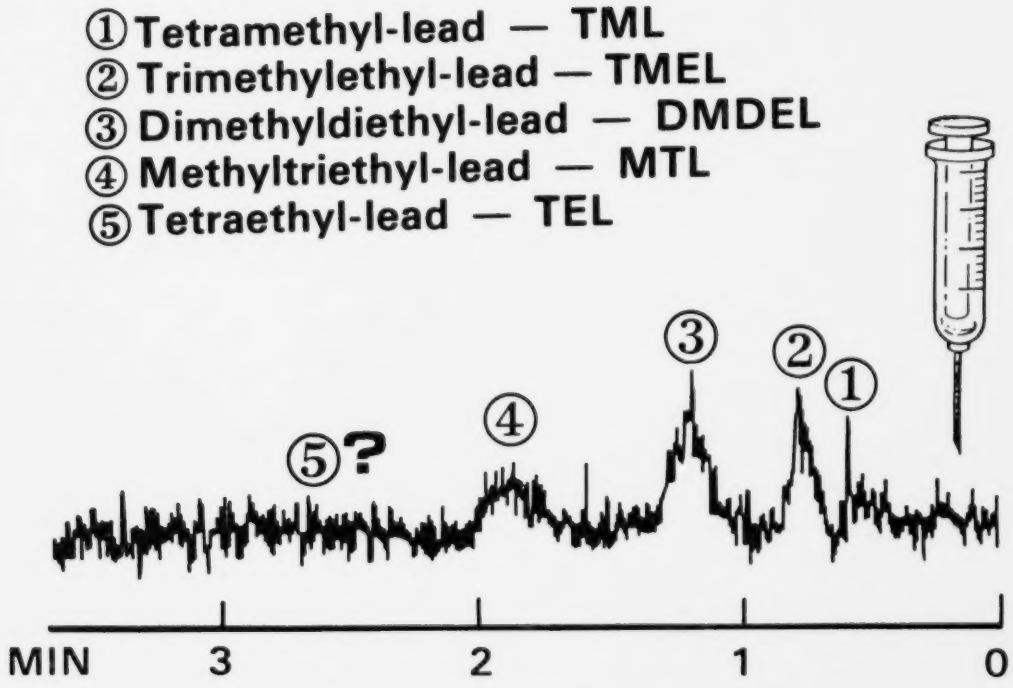

Figure 16. GC/AAS chromatogram of the spiked waste oil fuel by direct injection

for fuel, (1) a flue gas Pb concentration of 140 mg/m^3 and a waste oil concentration of about 3 g/l were found. These concentrations, total lead in waste oil fuel and flue gas discharge, are far above the demonstrated method detection limits for the GC/AAS method. If lead were appreciably present in an organometallic form in these samples, it should be measurable. These data indicate that organolead compounds could be only a minor constituent of the air atomizer discharges measured in this study. No organolead analyses were made on vaporizing pot burner emissions.

Organolead compounds have been estimated to be a small percentage (0.1-14%) of total ambient lead (22-24). Radziuk et al. (5) found that tailpipe emissions of alkyl lead are a minor fraction of ambient organolead levels. Volatile lead compounds in the ambient air arose from vaporization of gasoline and volatile lead losses from liquid fuels, not from combustion in internal combustion engines. The same effect would be expected from waste oil combustion. Waste crankcase oil combustion should be of minor concern for producing organolead emissions in the ambient air.

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APPENDIX A

XRF SPECTRA OF WASTE OIL SAMPLES

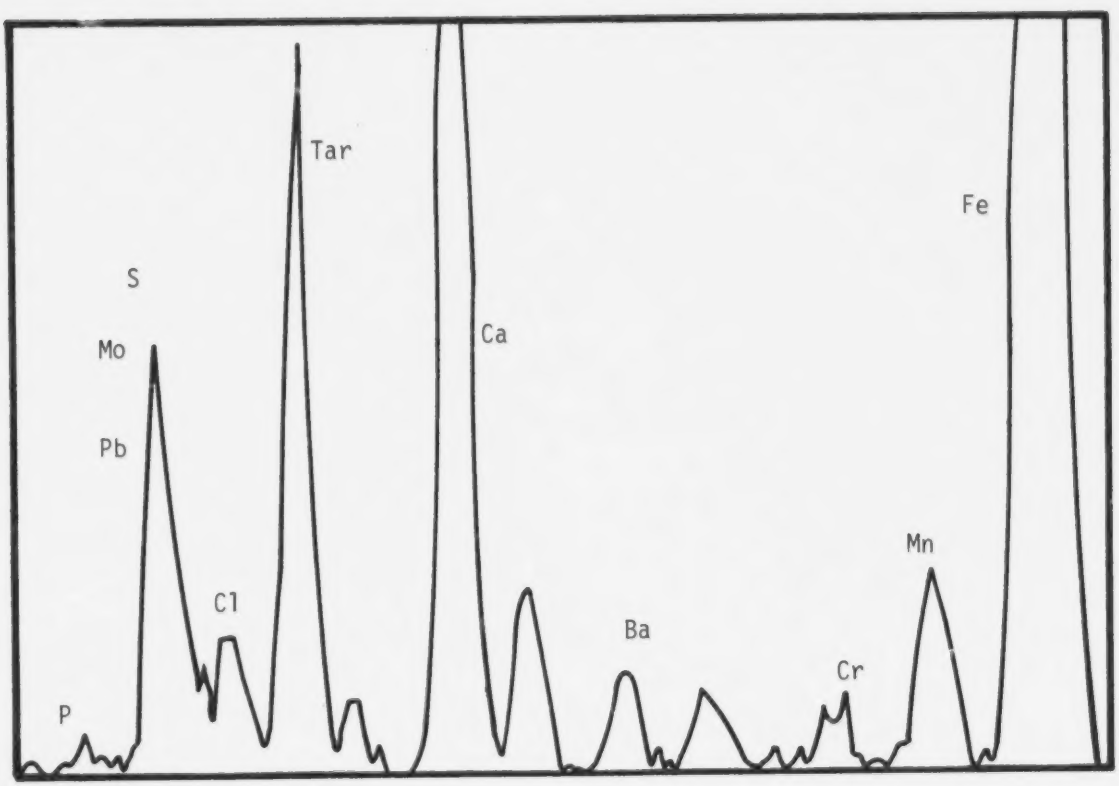

Figure A-1. Spectrum of waste oil sample AB using a Ge target.

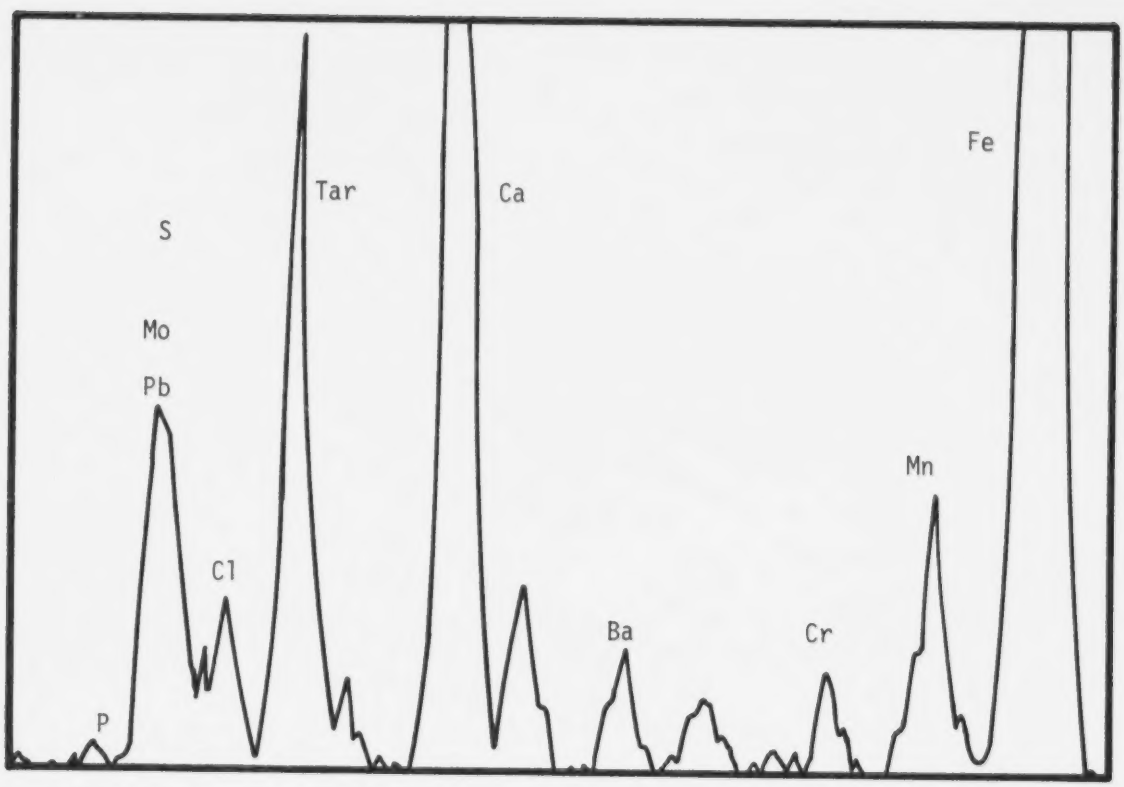

Figure A-2. Spectrum of waste oil sample AT using a Ge target.

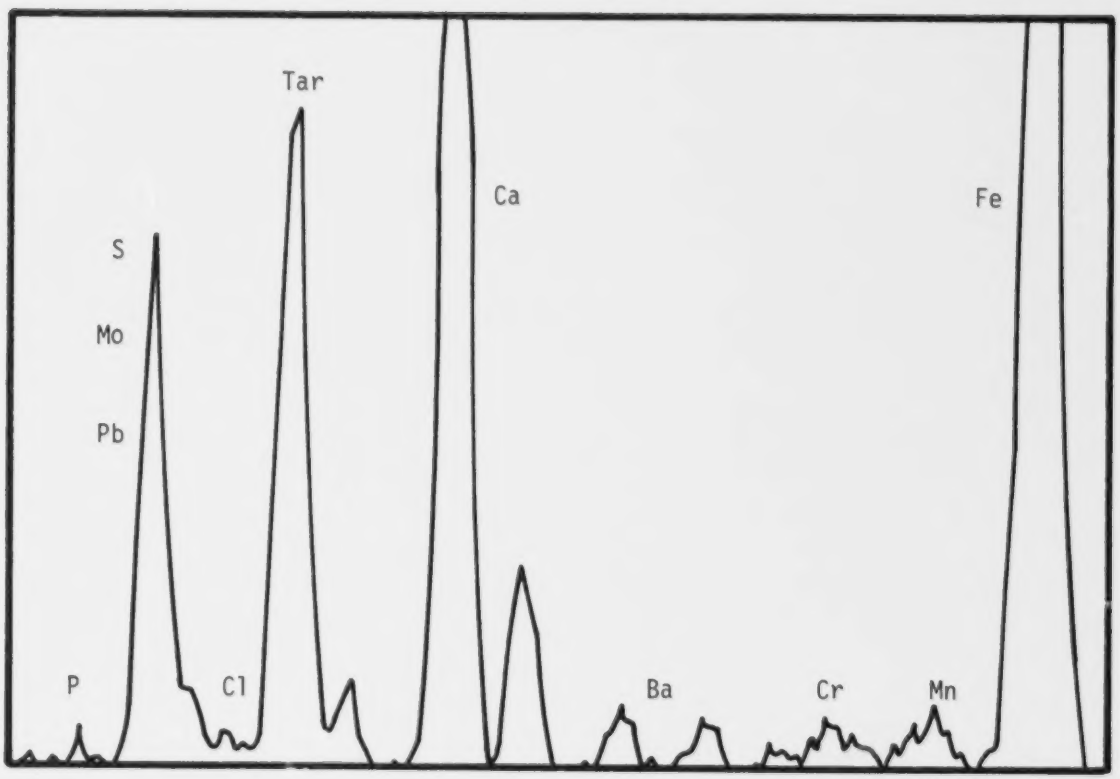

Figure A-3. Spectrum of waste oil sample TT using a Ge target.

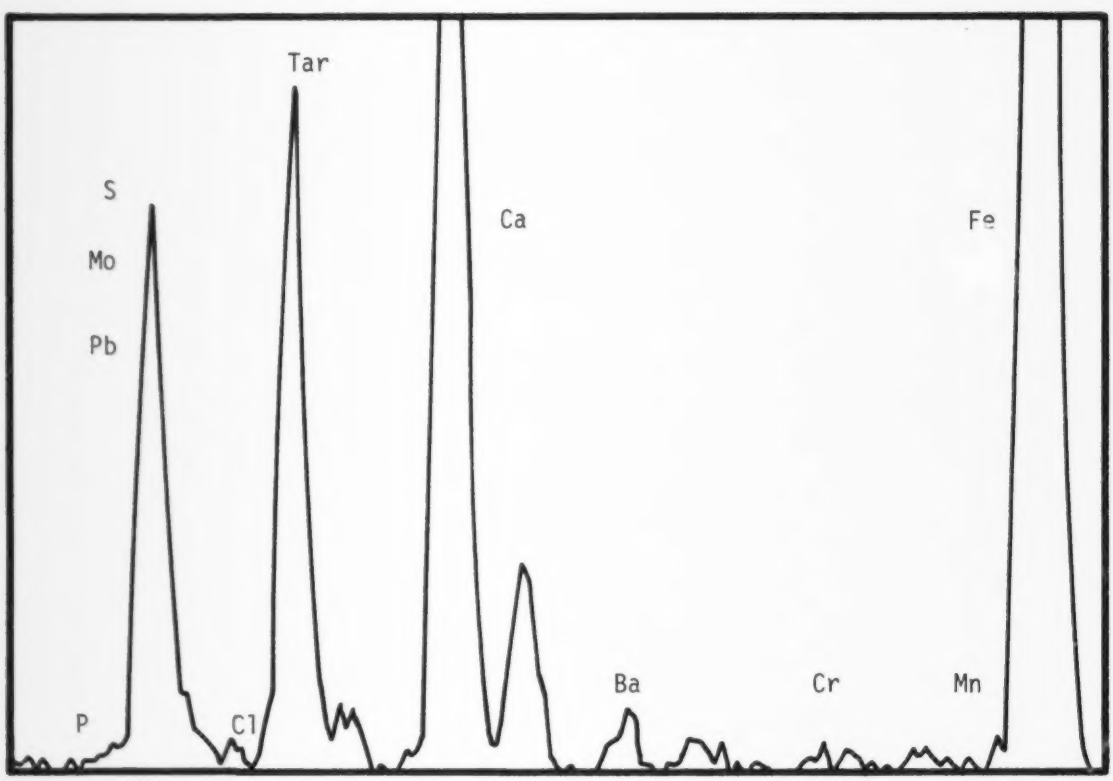

Figure A-4. Spectrum of waste oil sample TB using a Ge target.

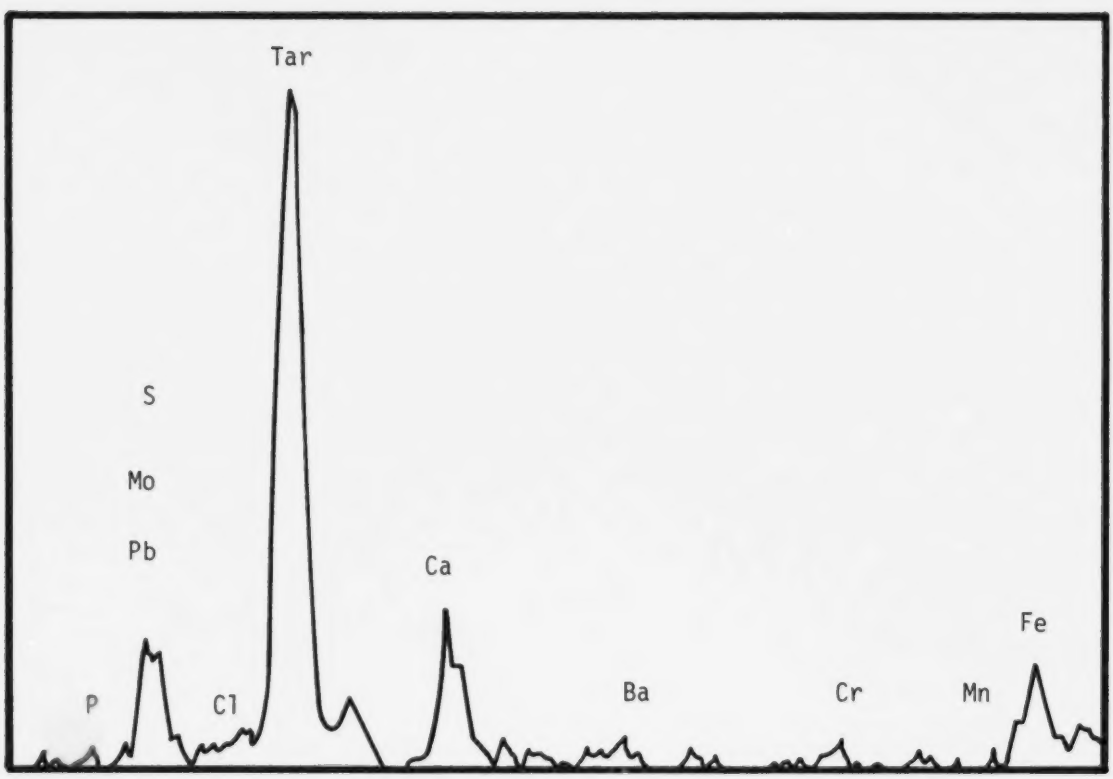

Figure A-5. Spectrum of waste oil sample DF using a Ge target.

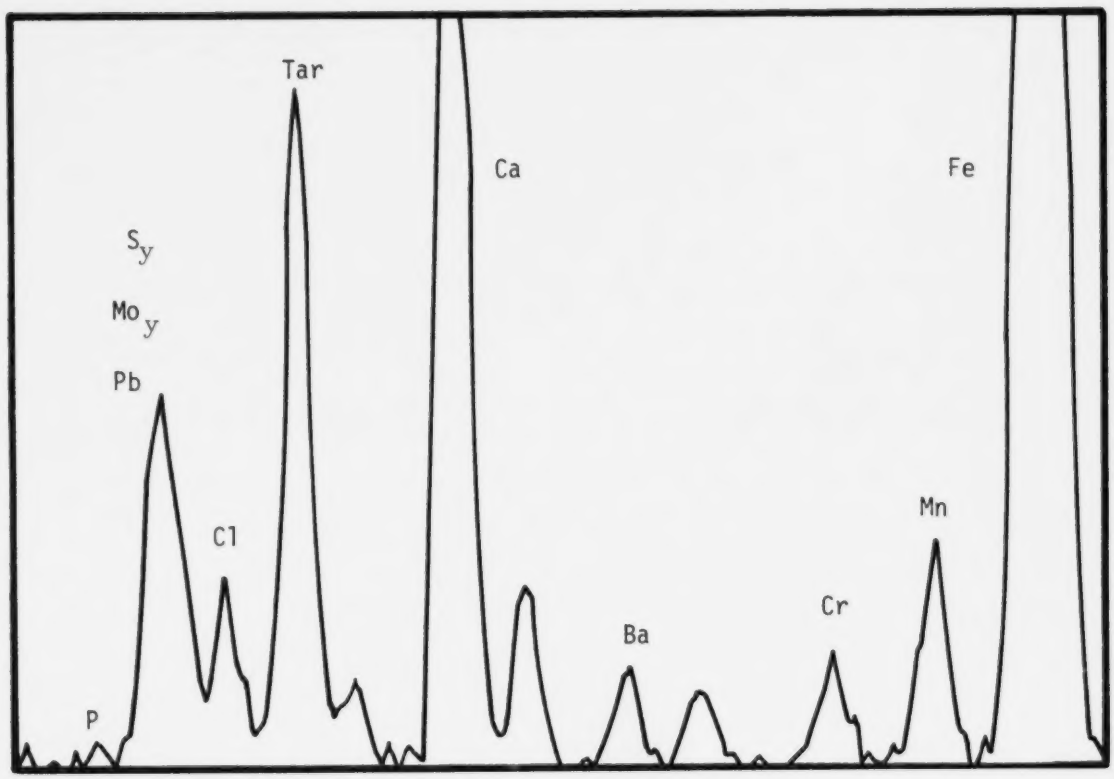

Figure A-6. Spectrum of waste oil sample MST2 using a Ge target.

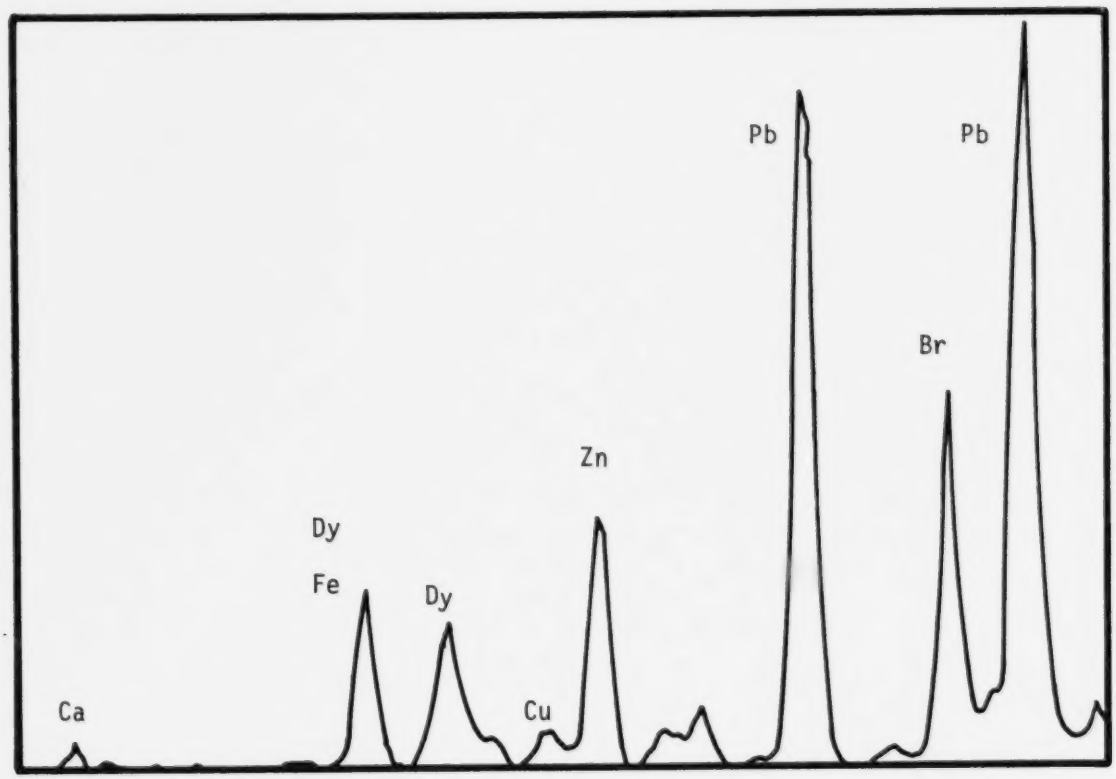

Figure A-7. Spectrum of waste oil sample MST2 using a Dy target.

APPENDIX B

XRF SPECTRA OF AIR ATOMIZER PARTICULATE DISCHARGES

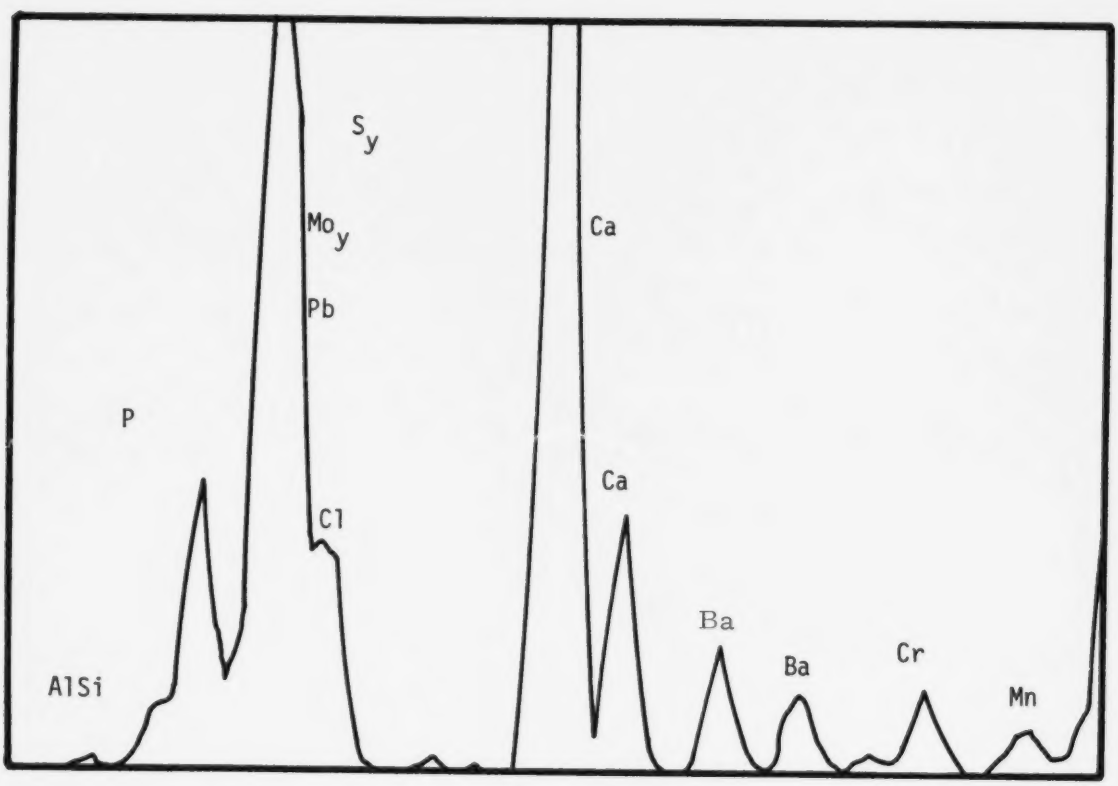

Figure B-1. Spectrum for particulate sample #5 using a Dy target.

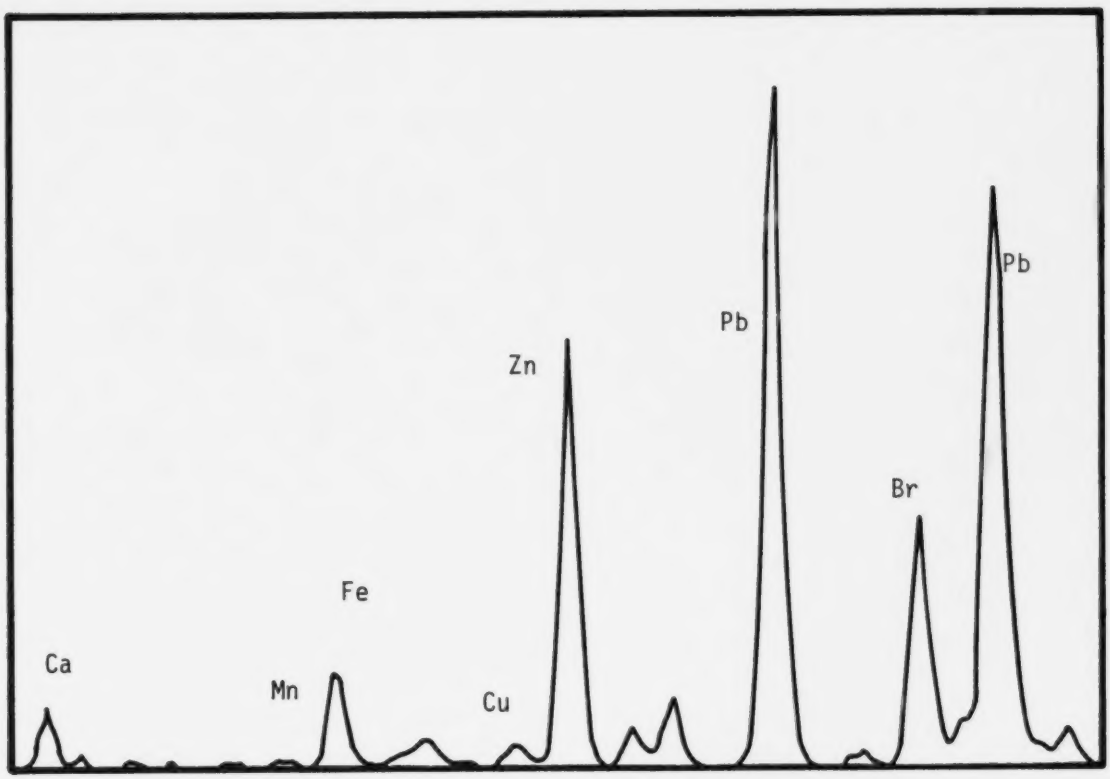

Figure B-2. Spectrum for particulate sample #5 using a Fe target.

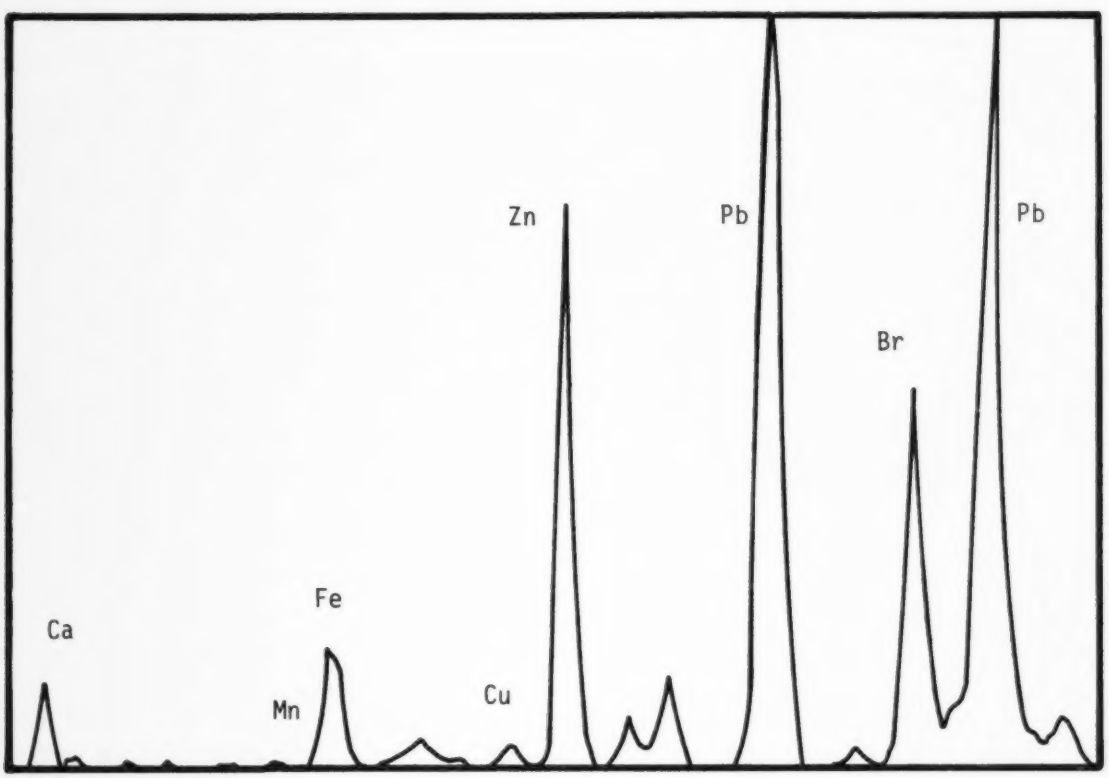

Figure B-3. Spectrum for particulate sample #6 using a Dy target.

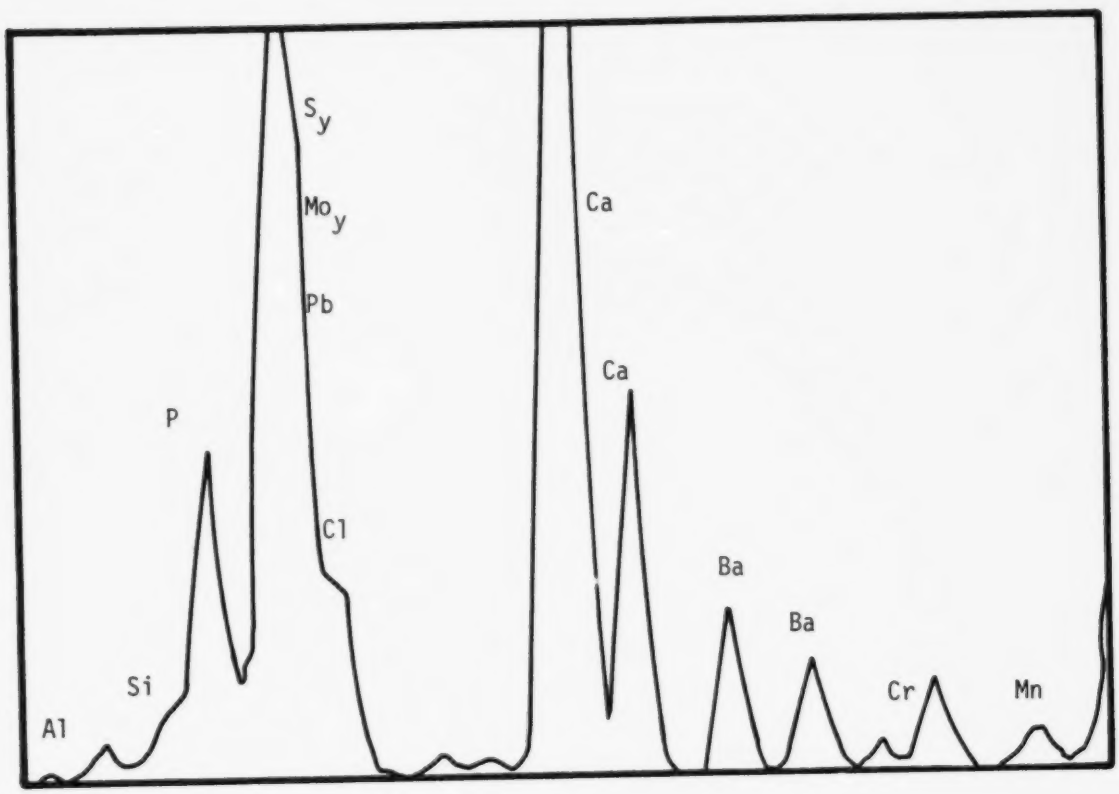

Figure B-4. Spectrum for particulate sample #6 using a Fe target.